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WADC TECHNICAL REPORT 55-221
PART III.
ASTIA DOCUMENT No. AD 118290

INVESTIGATION OF CONDENSATION TYPE ELASTOMERS

GEORGE C. SCHWEIKER
BURTON S. MARKS
RUSSELL R. WHITE
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HOOKER ELECTROCHEMICAL COMPANY

MAY 1957

WRIGHT AIR DEVELOPMENT CENTER

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MAY 1957

MATERIALS LABORATORY
CONTRACT No. AF 33(616)-2421
PROJECT No. 7340

WRIGHT AIR DEVELOPMENT CENTER
AIR RESEARCH AND DEVELOPMENT COMMAND
UNITED STATES AIR FORCE
WRIGHT-PATTERSON AIR FORCE BASE, OHIO

Carpenter Litho & Prtg. Co., Springfield, O.
500 - June 1957

FOREWORD

This report was prepared by the Hooker Electrochemical Company under USAF Contract No. AF 33(616)-2421. This contract was initiated under Project No. 7340, "Rubber, Plastic and Composite Materials", Task No. 73404, "Synthesis and Evaluation of New Polymers". The work was administered under the direction of the Materials Laboratory, Directorate of Research, Wright Air Development Center, with Lt. E.C. Stump and Capt. C.H. Schmid as project engineers.

This report covers work conducted from 1 December 1955 to 1 December 1956.

The personnel of the Hooker Electrochemical Company assigned to the project were Dr. George C. Schweiker, Research Supervisor, Dr. Burton S. Marks, and Mr. Russell R. White, Research Investigators, Mr. Rudolph N. Deleo, Technician, with Mr. P. Robitschek, Manager of Plastics Research acting as director.

ABSTRACT

The ultimate goal of the exploratory investigations described is the development of a rubber for special Air Force applications. High thermal stability (350°F or higher); resistance to aromatic fuels, synthetic ester-base oils and hydraulic fluids; resistance to ozone and to weathering oxidation effects; resistance to acids, bases, and salts; resistance to abrasion; and satisfactory performance at -65°F or lower are major requirements for such an elastomer.

Preliminary compounding and testing studies with an elastomer based on a fluorine-containing polyester, made from adipyl chloride and 2,2,3,3,4,4-hexafluoropentanediol, have given promising results. At the present stage of development, compounded and cross-linked specimens of hexafluoropentylene adipate retain useful mechanical properties after aging in air at 400°F (70 and 168 hour tests), and in diester oil at 350°F (70 hour test); are resistant to paraffinic and aromatic fuels; and exhibit a brittle temperature of -98°F (ASTM D-746).

This report describes the preparation, compounding, cross-linking and properties of hexafluoropentylene adipate elastomer as well as syntheses and properties of other fluorine-containing condensation polymers and difunctional starting materials. Data indicating that increasing fluorine content of the polymers decreases their solubility in common solvents without regard to position of the fluorine in the polymer are extended. On the other hand, these data show that position of the fluorine, rather than total fluorine content of the polymer is of most importance in affecting brittle temperatures.

PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDER:

R. T. Schwartz

R. T. SCHWARTZ
Chief, Organic Materials Branch
Materials Laboratory
Directorate of Research

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I. INTRODUCTION

In June of 1954, research on condensation type elastomers was started at Hooker Electrochemical Company under USAF Contract No. AF 33(616)-2421 with Materials Laboratory, Wright Air Development Center. Two summary reports have been written[1] which describe the research to December 1955 in detail. The present report covers the research performed from December 1955 to December 1956.

The ultimate goal of the work performed is the development of a rubber for special Air Force applications to possess a superior balance of properties. High thermal stability (350°F or higher); resistance to aromatic fuels, synthetic ester-base oils and hydraulic fluids; resistance to ozone and to weathering oxidation effects; resistance to acids, bases, and salts; resistance to abrasion; and satisfactory performance at -65°F or lower are major requirements for such an elastomer.

Presently available elastomers do not offer the combination of these desired properties. In the rubbers so far developed, one or more attributes have been attained only at the expense of some other important quality. A more detailed discussion, with references, of these points and of the reasons why certain fluorine-containing condensation elastomers were expected to exhibit a superior balance of properties has been given[1]. It has also been shown[1] that high molecular weight linear polyesters, which exhibit rubber-like properties, can be prepared from fluorine-containing diols, and that the polyesters can be cross-linked to give desirable elastomers.

Work during the current contract year, described in this report, has been concerned with the synthesis of new, and the preparation of known fluorine-containing intermediates considered desirable for polymerization; polymer syntheses and polymerization techniques; preliminary screening of properties; compounding and cross-linking of selected polymers; and preliminary testing and evaluation of promising elastomers. At the same time, of course, more data have been collected for the fundamental purpose of further relating and correlating physical properties of the polymers with chemical constitution.

Research on the synthesis of certain novel or unusual fluorine-containing intermediates considered desirable for polymerization in this project was performed at Purdue Research Foundation under subcontract to Hooker Electrochemical Company. Details of the syntheses performed at Purdue during the contract year comprise Appendix I of this report.

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II. SUMMARY AND CONCLUSIONS

The following fluorine-containing difunctional compounds have been prepared as intermediates or starting materials for use in polycondensation reactions.

1. Perfluoroglutaric Acid
2. Diethyl Perfluoroglutarate
3. Bis(N-methyl)perfluoroglutaramide
4. N-Methyl-4-carboethoxyperfluorobutyramide
5. 2,2,3,3,4,4-Hexafluoropentanediol
6. 2,2,3,3,4,4-Hexafluoropentane-1,5-bis(p-toluenesulfonate)
7. 2,2,3,3,4,4-Hexafluoropentane-1-ol-5-p-toluenesulfonate
8. Perfluoroadipic Acid
9. Diethyl Perfluoroadipate
10. 2,2,3,3,4,4,5,5-Octafluorohexanediol

Further syntheses leading to the preparation of fluorine-containing N-substituted diamines are currently under investigation; the products have not been completely characterized.

In addition to the above, research on the synthesis of other fluorine-containing difunctional compounds has been performed at Purdue Research Foundation under subcontract to Hooker Electrochemical Company, and the results of that work comprise Appendix I of this report.

Eight new fluorine-containing linear polyesters were made and their properties investigated. In accord with total fluorine content, those polymers having lower amounts of fluorine, i.e., hexafluoropentylene sebacate (30.2% F), are more soluble in common organic solvents than hexafluoropentylene adipate (35.4% F)[1b], while those polymers having greater amounts of fluorine, i.e., octafluorohexylene 3-perfluoroheptylglutarate (60.2% F) are less soluble in common organic solvents. Brittle temperatures of two of the polyesters, namely, hexafluoropentylene suberate and sebacate, are even lower than that of hexafluoropentylene adipate[1b], which indicates the feasibility of making a rubber with still superior low temperature properties. However, from the standpoint of making an elastomer with a superior balance of properties, hexafluoropentylene adipate is much preferred. Brittle temperatures of the 3-perfluoroheptylglutarates are 10-15° higher than the corresponding 3-perfluoropropylglutarates[1b], which demonstrates how brittle temperatures of the polyesters are increased by lengthening the fluorine-containing side chain.

The synthesis of certain polyesters previously prepared[1b] without using a high boiling solvent in the reaction mixture was re-examined. Both adipates and perfluoroadipates, prepared from the diacid chlorides and fluorine-containing diols, have been made with substantially increased molecular weights when the high boiling solvent technique was used. The molecular weights of corresponding glutarates and 3-perfluoroalkylglutarates, on the other hand, were increased by relatively small amounts.

Several larger batches of hexafluoropentylene adipate were prepared for compounding and testing, and samples of the gum as well as vulcanizates were submitted as directed by Materials Laboratory, Wright Air Development Center.

Compounding and testing studies show that high loadings of carbon black or a mixture of carbon black and calcium carbonate, together with tight cures are advantageous for imparting resistance of hexafluoropentylene adipate vulcanizates to aging in diester fluid at 350°F and in air at 400°F. For example, specimens of the linear polyester of number average molecular weight 15,600, when reinforced with a mixture of 60 parts black and 15 parts carbonate and cured with 20-22 parts of DI-CUP 40C (40% dicumyl peroxide on calcium carbonate) exhibited tensile strengths of 1000 to 1335 psi after 70 hours immersion in diester fluid at 350°F, and 940 to 1400 psi after 70 and 168 hours in air at 400°F. Weight losses and changes in elongation and hardness were relatively small.

Reinforcing agents other than carbon blacks, i.e., calcium carbonates, iron oxides, silicas, titanium dioxides, and diatomaceous earths, do not produce as heat resistant vulcanizates as do carbon blacks, although calcium carbonate reinforced vulcanizates are quite resistant to diester fluid at 350°F. A very preliminary study of common antioxidants indicated that they were not effective in amounts of 1 part by weight for imparting heat resistance in air at 400°F to the HAF black filled vulcanizates.

Weight losses of black reinforced hexafluoropentylene adipate vulcanizates at 350° and 400°F were small, but relatively higher weight losses were exhibited by the rubber after 150 hours in air at 450°F. Weight loss was further accelerated at 500°F.

Low temperature tests were performed at B.F. Goodrich Company on a black-reinforced vulcanizate of hexafluoropentylene adipate. The properties found are similar to those exhibited by natural rubber. The fluorinated elastomer had a brittle temperature (ASTM D-476) of -98°F; Gehman T_{10} was -62°F.

These data clearly indicate that low temperature flexibility need not be sacrificed in order to obtain fuel[1b] and diester fluid resistance, thermal stability, and good mechanical properties all combined in one elastomer.

III. DISCUSSION

A. SYNTHESIS OF STARTING MATERIALS

In keeping with the aims of the contract, and guided by past experimental work[1], emphasis has been centered, in the area of polyester synthesis, on preparing and using fluorine-containing diols with a variety of dicarboxylic acid chlorides as starting materials. The more readily available compounds of these classes have been made in the laboratories of the Hooker Electrochemical Company, and some hydrocarbon materials have been bought, with particular care placed on their purity.

Recently, laboratory investigations have been initiated on possible methods of synthesizing fluorine-containing N-substituted diamines for use as starting materials in the area of polyamide synthesis.

The following fluorine-containing difunctional compounds have been prepared during the period of time covered by this report.

1. Perfluoroglutaric Acid
2. Diethyl Perfluoroglutarate
3. Bis(N-methyl)perfluoroglutaramide
4. N-Methyl-4-carboethoxyperfluorobutyramide
5. 2,2,3,3,4,4-Hexafluoropentanediol
6. 2,2,3,3,4,4-Hexafluoropentane-1,5-bis(p-toluenesulfonate)
7. 2,2,3,3,4,4-Hexafluoropentane-1-ol-5-p-toluenesulfonate
8. Perfluoroadipic Acid
9. Diethyl Perfluoroadipate
10. 2,2,3,3,4,4,5,5-Octafluorohexanediol

In addition, research on the synthesis of other fluorine-containing difunctional compounds has been performed at Purdue Research Foundation under subcontract to Hooker Electrochemical Company, and the results of that work comprise Appendix I of this report.

Perfluoroglutaric acid was prepared by aqueous permanganate oxidation of 1,2-dichlorohexafluorocyclopentene (Hooker Electrochemical Company) according to the method described by McBee, Wiseman and Bachmann[2]. Perfluoroadipic acid[2] was made similarly from 1,2-dichlorooctafluorocyclohexene. Esterification of the acids, followed by reduction of the esters[2] with lithium aluminum hydride (Metal Hydride, Inc.) as described by McBee, Marzluff and Pierce[3] gave 2,2,3,3,4,4-hexafluoropentanediol and 2,2,3,3,4,4,5,5-octafluorohexanediol, respectively.

Reaction of 2,2,3,3,4,4-hexafluoropentanediol with p-toluenesulfonyl chloride gave 45-65% yields of 2,2,3,3,4,4-hexafluoropentane-1,5-bis(p-toluenesulfonate). From this reaction, small amounts of 2,2,3,3,4,4-hexafluoropentane-1-ol-5-p-toluenesulfonate have been isolated. An earlier report in Appendix I of reference 1a, concerning the mono and ditosylates of the fluorine-containing diol is in error.

Bis(N-methyl)perfluoroglutaramide was synthesized in 70% yield from reaction of methylamine with diethyl perfluoroglutarate. About 9% yield of N-methyl-4-carboethoxyperfluorobutyramide was also isolated from this reaction.

Reaction of 2,2,3,3,4,4-hexafluoropentane-1,5-bis(p-toluenesulfonate) with methylamine at 165°C gave a mixture of products from which a small amount of N-methyl-p-toluenesulfonamide and a solid, m.p. 146.5-147°C, have been isolated. The solid contains nitrogen and sulfur, but its structure is at present unknown.

Reduction of bis(N-methyl)perfluoroglutaramide to 2,2,3,3,4,4-hexafluoropentane-1,5-bis(N-methylamine) is currently under investigation. A preliminary hydrogenation, initial hydrogen pressure of 2500 psi, with methylamine added to the bomb, was run at 175°C with 11% of a mixed catalyst containing copper chromite and a small amount of Raney nickel. A large amount of starting material was recovered along with a small amount of yellow oil. Redistillation of the oil gave colorless liquid, b.p. 53°C/1.6 mm, which crystallized to a white, low melting solid. Infra-red spectra showed that the amide group was still present, along with a new NH function, as well as increased CH_2 frequency, which indicates that the low-melting solid may be the mono-reduction product of bis(N-methyl)perfluoroglutaramide.

An attempt to determine whether fluorine-containing N-substituted diamines could be prepared via an interesting reaction performed with hydrocarbon alcohols and amines[4-7] was investigated using 2,2,3,3,4,4-hexafluoropentanediol and aniline. The reaction consisted of heating a mixture of the diol, aniline, and a small amount of sodium to give the monc-sodium salt of the diol, with Raney nickel. Preliminary indications are that some reaction appeared to occur through the dehydrogenation and addition of aniline to the aldehyde, with loss of water, stages to give a Schiff base, at least on one end of the diol, since hydrogen and a small amount of water were evolved. On working up the reaction mixture, starting materials and a small amount of yellow oil, b.p. 100°C/2.5 mm, was isolated; interpretation of infra-red spectra of the oil appears to be consistent with the structure $HOCH_2(CF_2)_3CH = NC_6H_5$.

B. LINEAR POLYESTERS

Previous work[1] has shown that the best method of synthesizing high molecular weight polyesters from fluorine-containing diols is through the use of dicarboxylic acid chlorides and the diols. Accordingly, eight new polyesters were synthesized by this method, and their properties investigated. It has been found that the use of a high boiling liquid such as dichlorobenzene in the reaction mixture raises molecular weights of certain polyesters even higher than that previously attained[1b]. Consequently, the synthesis of a number of polyesters, previously prepared[1b], was re-examined.

Table I summarizes the data on the properties of the linear polyesters. The first column lists the reactants used; the second column lists the melt viscosities (η) of the polymers produced. The various functions of the viscosities, i.e., number average molecular weight (M_n), degree of polymerization (x_n), weight average chain length (Z_w) were calculated from Flory's equations, used by him in the hydrocarbon polyester series[8], using constants determined previously[1] during the course of this work. These functions are subject to the limitations already discussed. Columns six and seven list the approximate melting and brittle temperatures, respectively, of the polyesters; column eight contains information on their solubilities in various liquids.

The new polyesters prepared from the fluorine-containing diols and hydrocarbon dicarboxylic acid chlorides do not show any unusual characteristics. Solubility in common liquids is increased somewhat for these polyesters in accord with expectations based on the decreased total fluorine content of the compounds. The most notable increase in solubility is that shown to benzene. This behaviour, of course, is undesirable from the standpoint of making solvent resistant elastomers.

The polyesters containing a fluorinated side chain (i.e., those made from the acid chlorides, 3-perfluoropropylglutaryl chloride[1b] and 3-perfluoroheptylglutaryl chloride[1b], synthesized at Purdue University under subcontract to Hooker Electrochemical Company) exhibit increased solvent resistance in accord with increased total fluorine content of the polymers.

Table II illustrates in a general way how solubility of some of these polyesters decreases with increasing total fluorine content. The range of fluorine content of the polymers is from 30.2% F in the case of hexafluoropentylene sebacate to 60.2% F in the case of octafluorohexylene 3-perfluoroheptylglutarate.

Of the polyesters listed in Table I, only hexafluoropentylene suberate and sebacate exhibit brittle temperatures lower than that found for hexafluoropentylene adipate. And for the purpose of making an elastomer with an especially low brittle point, hexafluoropentylene suberate would appear to be admirably suitable. However, since hexafluoropentylene adipate has a very low brittle temperature, and at the same time has other superior properties, from the standpoint of making an elastomer with a superior balance of properties, the adipate is much preferred.

TABLE I

POLYESTERS FROM DICARBOXYLIC ACID CHLORIDES AND FLUORINE-CONTAINING DIOLS

Reactants		Melt Viscosity (η) poises; °C	No. Ave. Mol. Wt. (M_n)	Degree of Polym. (x_n)	Wt.Ave. Chain Length (Z_w)	Approx. Brittle Temp(°C)	Approx. m.p. (°C)	Solubility* (0.1g/3cc)
$(CH_2)_3(COCl)_2$	$(CF_2)_3(CH_2OH)_2$	191 (100°)	7,930	51.3	614	-50° to -55°	40°	Sol: A,CH,P,EA Insol: B(d),T,I,2Ol, W,E,XHF
$(CH_2)_3(COCl)_2$	$(CF_2)_4(CH_2OH)_2$	239 (110°)	8,950	50.0	646	-50° to -55°	40°	Sol: A,CH,P(d),EA,BTF Insol: B(d),T,I,2Ol, W,E,XHF(d)
$(CH_2)_4(COCl)_2$	$(CF_2)_3(CH_2OH)_2$	23,000 (205°)	25,000	155	2010	-65°	30°	Sol: A,EA,CH,B,P Insol: T,I,2Ol,C,W
$(CH_2)_4(COCl)_2$	$(CF_2)_4(CH_2OH)_2$	6,380 (215°)	24,000	129	1800	-	60-70°	Sol: A,EA,CH,P Insol: B,T,I,2Ol,C,W
$(CH_2)_6(COCl)_2$	$(CF_2)_3(CH_2OH)_2$	225 (110°)	7,480	42.7	636	-75°	20-26°	Sol: A,EA,T,CH,B,P Insol: I,2Ol,C,W
$(CH_2)_6(COCl)_2$	$(CF_2)_4(CH_2OH)_2$	340 (110°)	8,800	44.0	698	-	58-61°	Sol: A,EA,CH,B,T,P Insol: I,2Ol,C,W
$(CH_2)_7(COCl)_2$	$(CF_2)_3(CH_2OH)_2$	2,790 (110°)	12,000	66.0	1050	-48° to -65°	30°	Sol: A,EA,CH,B,T,P Insol: I,2Ol,C,W
$(CH_2)_7(COCl)_2$	$(CF_2)_4(CH_2OH)_2$	3,440 (110°)	13,300	64.3	1085	-	47-50°	Sol: A,EA,CH,B,T,P Insol: I,2Ol,C,W
$(CH_2)_8(COCl)_2$	$(CF_2)_3(CH_2OH)_2$	1,900 (110°)	11,000	58.1	980	below -65°	30°	Sol: A,EA,CH,B,T,P Insol: I,2Ol,C,W
$(CH_2)_8(COCl)_2$	$(CF_2)_4(CH_2OH)_2$	115 (110°)	6,580	30.7	544	-	55-60°	Sol: A,EA,CH,B,T,P Insol: I,2Ol,C,W

TABLE I (cont'd)

POLYESTERS FROM DICARBOXYLIC ACID CHLORIDES AND FLUORINE-CONTAINING DIOLS

Reactants		Melt Viscosity (η) poises; °C	No. Ave. Mol. Wt. (M_n)	Degree of Polym. (x_n)	Wt. Ave. Chain Length (Z_w)	Approx. Brittle Temp(°C)	Approx. m.p. (°C)	Solubility* (0.1g/3cc)
$(CF_2)_4(COCl)_2$	$(CF_2)_3(CH_2OH)_2$	475 (110°)	13,500	58.0	750	-55° to -58°	35°	Sol: A,E,EA,BTF,XHF Insol: T,B,CH,I,201, P(a), W(a)
$(CF_2)_4(COCl)_2$	$(CF_2)_4(CH_2OH)_2$	700 (110°)	15,000	58.2	810	-	65-70°	Sol: A,E,EA,BTF, XHF Insol: T,B,CH,I,201, P(a), W(a)
$C_3F_7CH(CH_2COCl)_2$	$(CF_2)_3(CH_2OH)_2$	37 (110°)	9,000	34.2	405	-25° to -30°	-	Sol: A,E,EA,BTF,XHF Insol: B,T,I,201,W, P(d), CH(d)
$C_3F_7CH(CH_2COCl)_2$	$(CF_2)_4(CH_2OH)_2$	51 (110°)	9,940	34.5	442	-25° to -30°	-	Sol: A,E,EA,BTF,XHF Insol: B,T,I,201,W P(d), CH(d)
$C_7F_{15}CH(CH_2COCl)_2$	$(CF_2)_3(CH_2OH)_2$	21.9 (110°)	9,920	29.3	347	-15° to -20°	-	Sol: A,EA,BTF,XHF Insol: CH,B,T,I,201, C,P,W
$C_7F_{15}CH(CH_2COCl)_2$	$(CF_2)_4(CH_2OH)_2$	27.1 (110°)	10,400	28.8	369	-15° to -20°	-	Sol: A,EA,BTF,XHF Insol: CH,B,T,I,201, C,P,W

* A = acetone
EA = ethyl acetate
CH = chloroform
201 = diester (Plexol 201)
C = carbon tetrachloride
I = isooctane
P = pyridine
W = water
BTF = benzotrifluoride
T = toluene
XHF = xylenehexafluoride
B = benzene
(d) = dispersed
(a) = attacked

TABLE II

DECREASING SOLUBILITY OF FLUORINE-CONTAINING POLYESTERS WITH INCREASING FLUORINE CONTENT

Polyester	No.Ave. Mol.Wt. (M_n)	Degree of Polym. (x_n)	Wt.Ave.Chain Length (Z_w)	% F (Ca.)	*Solubility (0.1g/3cc) Benzene	Toluene	Chloro-form	Iso-octane	Plexol 201
$[OCH_2(CF_2)_3CH_2O_2C(CH_2)_8CO]_n$	11,000	58.1	980	30.2	+	+	+	-	-
$[OCH_2(CF_2)_3CH_2O_2C(CH_2)_4CO]_n$	25,000	155	2010	35.4	+	-	+	-	-
$[OCH_2(CF_2)_4CH_2O_2C(CH_2)_4CO]_n$	24,000	129	1800	40.6	-	-	+	-	-
$[OCH_2(CF_2)_4CH_2O_2C(CH_2)_3CO]_n$	6,600	25.1	427	41.4	-	-	+	-	-
$[OCH_2(CF_2)_3CH_2O_2CCH_2\underset{C_3F_7}{C}HCH_2CO]_n$	7,860	33.0	392	51.9	-	-	±	-	-
$[OCH_2(CF_2)_3CH_2O_2C(CF_2)_4CO]_n$	13,500	58.0	750	57.1	-	-	-	-	-
$[OCH_2(CF_2)_4CH_2O_2C(CF_2)_4CO]_n$	15,000	58.2	810	58.9	-	-	-	-	-
$[OCH_2(CF_2)_4CH_2O_2CCH_2\underset{C_7F_{15}}{C}HCH_2CO]_n$	10,400	28.8	369	60.2	-	-	-	-	-

* Room temperature solubility: + soluble; - insoluble

Figure 1 illustrates melting and brittle temperatures of some of the polyesters listed in Table 1. The familiar zig-zag curve of odd-even numbered atoms in the chain unit is evident, especially for the polymers prepared from the even numbered diol, 2,2,3,3,4,4,5,5-octafluorohexanediol. The polyesters in Figure 1, prepared from this diol and straight chain dicarboxylic acid chlorides crystallized so quickly that it was impossible to measure their brittle temperatures, with the exception of octafluorohexylene glutarate. The higher melting points and rate and degree of crystallization of these polyesters indicate that they are unsuitable as homopolymers for the purpose of making elastomers. Of the polyesters in Figure 1 prepared from 2,2,3,3,4,4-hexafluoropentanediol and straight chain dicarboxylic acid chlorides, however, two polymers as discussed above exhibited lower brittle temperatures than that of hexafluoropentylene adipate. The very large range recorded for the brittle temperature of hexafluoropentylene azelate is because this polyester crystallized much more readily than the others made from 2,2,3,3,4,4-hexafluoropentanediol, and during the examination, it generally crystallized before reaching its true brittle temperature.

Figure 2 illustrates the effect of fluorine content and position in the molecule on melting and brittle temperatures of some polyesters. The polymers containing fluorinated side chains could not be induced to crystallize, because the appended groups act to either prevent normal packing or to increase vibration interaction of interlocking molecules. The effect of fluorinated side groups on brittle temperatures is shown in Figure 2 for the glutarate polyester series. The perfluoropropyl group appended to the polymers by using 3-perfluoropropylglutaryl chloride in their synthesis results in a raising of their brittle temperatures by 20-25°C over the corresponding unsubstituted glutarate polyesters. When the length of the side group is increased to perfluoroheptyl, the brittle temperatures of the polymers are raised some 30-35°C higher than the corresponding unsubstituted glutarates. These examples demonstrate that brittle temperatures of the polyesters are increased by the presence of a fluorinated side chain, and that with increasing length of the side chain, brittle temperatures are further increased.

On the other hand, increasing the fluorine content of the polyesters in the adipate series, by attaching additional fluorine atoms on the backbone chain of the polyesters, as shown in Figure 2 with hexafluoropentylene perfluoroadipate, raised the brittle temperature of the polymer by only about 10°C over the corresponding hexafluoropentylene adipate. Melting points of the perfluoroadipates were elevated by less than 10°C. In the case of hexafluoropentylene 3-perfluoroheptylglutarate, total fluorine content of the polyester (59.0% F) was increased by 22% over the corresponding unsubstituted glutarate with an increase of 30-35°C in brittle temperature. In the case of hexafluoropentylene perfluoroadipate (57.1% F), total fluorine content of the polyester was increased by 21.7% over the corresponding adipate with an increase of only about 10° in brittle temperature. These data forcibly demonstrate that position of the fluorine atoms in the polymers is much more important than total fluorine content, in affecting brittle temperatures of the polyesters.

Further consideration of Table I shows that the highest molecular weight (M_n) and degree of polymerization (x_n) is obtained with adipyl chloride and the fluorine-containing diols. The use of a high boiling solvent such as dichlorobenzene in the reaction mixture increased the molecular weights of polyesters reported previously[1b], made in the absence of high boiling solvent. The most notable change in the properties of hexafluoropentylene adipate of increased molecular weight (M_n 25,000) was in the increased tensile strength of its gum vulcanizates (Section C of this report), and, of course, in increased viscosity. The molecular weights of octafluorohexylene adipate (M_n 24,000) and of the perfluoroadipates listed in Table I were also significantly increased over those obtained previously[1b]. Because the polyesters made from perfluoroadipyl chloride and from the 3-perfluoroalkylglutaryl chlorides are insoluble in dichlorobenzene, the high boiling solvent used in their reactions with the fluorine-containing diols was dichlorohexafluoroxylene. Molecular weights of polyesters prepared from the five-carbon-chain dicarboxylic acid chlorides were also raised, but not nearly as much as in the case of the adipates and perfluoroadipates. It was disappointing, but not unexpected, to find that the perfluoroadipates, even at these higher molecular weights (13,500-15,000), were still attacked by water. Although the perfluoroadipates visibly appear to be unaffected by water, the pH of the surrounding water decreases to approximately 1 after several days immersion. This susceptibility to hydrolytic attack is caused by the strong inductive effect of the difluoromethylene moiety alpha to the ester carbonyl as previously discussed[1].

During the period of time covered by this report, larger amounts of hexafluoropentylene adipate were prepared for compounding and testing, and samples of the gum rubber were submitted as directed by Materials Laboratory, Wright Air Development Center.

C. CROSS-LINKING, REINFORCING, AND PROPERTIES OF HEXAFLUOROPENTYLENE ADIPATE VULCANIZATES

As noted previously[1b], tensile strength of gum vulcanizates of hexafluoropentylene adipate, cured with dicumyl peroxide, increases markedly with increasing molecular weight (M_n) of the linear polyester. Figure 3 illustrates that this effect is still operating at M_n up to 25,000. The slope of the curve relating tensile strength of gum vulcanizates to M_n of linear polyester, however, is much lower at M_n of 25,000 than it is at M_n of 12,000, and it is apparent that increase in tensile strength with still higher M_n would be relatively slight. It should be noted that the increase in tensile strength with increasing M_n does not apply in this range to reinforced vulcanizates, since even relatively low molecular weight polyester vulcanizates have respectably high tensile strengths when any one of several reinforcing agents have been used.

Results of heat aging and low temperature tests with an early compounding recipe of hexafluoropentylene adipate vulcanizates are shown in Table III. The linear polyester had molecular weights of 17,100 and 18,400; reinforcing agent was 20 parts HAF black (Philblack O); curing agent was 11 parts DI-CUP 40C (a mixture of 40% dicumyl peroxide on calcium carbonate); cure, 50 minutes at 160°C. Weight losses listed in Table III are the significant factors in this preliminary evaluation of thermal stability. At 350° and 400°F, relatively small weight losses are recorded. The fact that weight loss between 70 and 150 hours at 400°F is small indicates that the base material is only slightly effected during extended periods of time in air at this temperature. Weight loss increases fairly rapidly with length of time at 450°F, however, which indicates that this temperature is close to the upper limit to be withstood by the elastomer. Weight loss at 500°F for 24 hours is high.

Table III includes low temperature properties of the compound as determined at B F Goodrich Company. The very low brittle temperature (ASTM D-746) of -98°F and Gehman T_{10} of -62°F indicate the potentiality of the elastomer for low temperature uses in conjunction with its indicated potential for thermal stability and fuel[1b] and diester fluid resistance. The Gehman curve for the compound is given in Figure 4. We are grateful to A E Juve, Director, Technical Service Research, B F Goodrich Company for the low temperature tests data. The low temperature characteristics exhibited by the hexafluoropentylene adipate elastomer are strikingly similar to those manifested by natural rubber.

Results of aging at room temperature in various fluids, including 70/30: isooctane/toluene and Plexol 201 (Diester fluid), have previously[1b] been shown to be good for HAF black reinforced hexafluoropentylene adipate. The following data show that the elastomer is resistant as well to JP-4 fuel (same compounding recipe as shown for Table III).

PROPERTIES AFTER AGING IN JP-4 FUEL AT ROOM TEMPERATURE

Time(hrs.)	Wt.Gain(%)	Tens.(psi)	Elong.(%)	300% Mod.(psi)	Set(%)	Hard.(Shore A)
70	2.0	3395	325	3100	1-2	70-73
168	2.6	2950	325	2565	1-2	69-72

TABLE III

HIGH AND LOW TEMPERATURE PROPERTIES OF HEXAFLUOROPENTYLENE ADIPATE CARBON BLACK VULCANIZATES
(20 parts Philblack O, 11 parts DI-CUP 40C)

Thermal Stability*

Test Temperature (°F)	350°	350°	350°	400°	400°	450°	450°	450°	500°
Time (hours)	24	168	257	70	150	24	70	150	24
Weight Loss (%)	1.58	2.62	3.04	4.5	6.3	5.4	12.3	23.8	17.7
Tensile Strength (psi)	-	-	1265	720	640	341	320	385	80
Elongation (%)	-	-	400	225	325	350	300	125	200
300% Modulus (psi)	-	-	750	-	-	262	320	-	-
Set at Break (%)	-	-	2-3	3-4	5-6	9	13	5-6	18-19
Hardness (Shore A)	-	-	63-67	62-65	62-64	60-63	63-65	68-72	52-55

Low Temperature Properties+

Brittle Temperature ASTM D-746..... -98°F
Gehman T_2..... -42°F
T_5..... -56°F
T_{10}..... -62°F
T_{100}..... -72°F

Freeze point..... -71°F
Torsional Modulus (G) at room temperature..... 188 psi

*Heat aging tests performed on 0.025" thick dumbbell specimens.

+Low temperature properties obtained from A E Juve, Director, Technical Service Research, B F Goodrich Company

After 168 hours in MIL-O-5606 fluid at 316°F, however, this compound became sticky and very weak.

Physical properties of hexafluoropentylene adipate of a higher molecular weight stock (M_n 25,000), when compounded as above, were not changed significantly from that previously reported[1b] for lower molecular weight vulcanizates.

A very preliminary study of six common antioxidants used at a concentration of 1 part by weight in the above compounding recipe indicated that they did not significantly increase resistance of vulcanizates to air at 400°F or to diester fluid at 350°F. In several cases, properties of the aged vulcanizates containing antioxidant were significantly worse than the control, but this is probably due to a lower degree of cure, since the same amount of peroxide curing agent was used both with and without antioxidant (i.e., no effort to compensate for reaction of antioxidant with peroxide was made). The antioxidants so used were: neozone D, phenothiazine, permalux, agerite resin D, agerite white, aminox.

Other reinforcing agents were also screened to determine if better thermal stability in air and in Plexol 201 could be obtained with hexafluoropentylene adipate vulcanizates. At loadings of 20 and 40 parts, all non-black fillers tested, which included calcium carbonates, iron oxides, silicas, titanium dioxides, and diatomaceous earths, gave very poor vulcanizates for resistance to air at 400°F. The carbonate filled vulcanizates were better than correspondingly loaded carbon black vulcanizates, however, in their resistance to aging in Plexol 201 at 350°F.

Among the carbon blacks screened at loadings of 20 and 40 parts, FEF black (Philblack A) and SRF black (Furnex) gave the best retention of properties to their vulcanizates after aging in air at 400°F and in Plexol 201 at 350°F. From these screening tests, it became evident that loadings of 40 parts gave better retention of properties to aged vulcanizates, than loading of 20 parts, in general, for both black and non-black filled rubbers. Original unaged tensiles were usually slightly lower for the former vulcanizates, however, than for the latter.

The effects of higher loadings and tighter cures of hexafluoropentylene adipate vulcanizates were examined with Furnex, Philblack A, Purecal U (calcium carbonate), and mixtures of Purecal U with these blacks. Table IV lists the most recent results obtained. In Table IV, original mechanical properties, together with percent weight loss and properties after aging in air at 400°F and in Plexol 201 at 350°F are shown. The gum rubber used was hexafluoropentylene adipate of molecular weights 15,600 and 15,700. Sheets were cured for 50 minutes at 160°C. From the standpoint of tensile strength exhibited by the vulcanizates after aging in air at 400°F, and in Plexol 201 at 350°F, the best vulcanizates yet examined were those containing a mixture of 60 parts black and 15 parts carbonate cured with 20-22 parts DI-CUP 40C. Tensiles of from 940 to 1400 psi after aging 70 and 168 hours in air at 400°F, and in Plexol 201 for 70 hours at 350°F were exhibited

by these vulcanizates. The data in Table IV also indicate that the beneficial effects caused by tighter cures and higher loadings, as exhibited by aged vulcanizates, may be obtained with proper carbonate-black mixtures, in part reducing the effects of low elongation and high hardness caused by highly loaded carbon black vulcanizates.

TABLE IV

PROPERTIES OF HEXAFLUOROPENTYLENE ADIPATE VULCANIZATES

Reinforcing Agent (Parts by Weight)	Curing Agent (Parts by Weight)	Original Properties				Aged Properties; Plexol 201 at 350°F, 70 hours immersion				
		Tensile (psi)	Elongation (%)	Set at Break (%)	Hardness (Shore A)	% Wt Loss	Tensile (psi)	Elongation (%)	Set at Break (%)	Hardness (Shore A)
60 Furnex + 15 Purecal U	20 DI-CUP 40C	2120	125	0-1	78-81	5.5	1335	150	3-4	67-8
" "	22 " " "	2180	100	0-1	82-4	4.9	1000	75	1-2	71-3
60 Philblack A + 15 Purecal U	20 " " "	2390	100	0-1	83-6	6.2	1040	100	6-7	76-8
" "	22 " " "	1950	75	0-1	85	6.3	1000	100	3-4	77-9
50 Philblack A + 10 Purecal U (M_n 15,600)	17 " " "	1960	125	0-1	76-8	4.0	1335	150	6-7	65-8
Purecal U (M_n 15,700)	17 " " "	2130	150	0-1	69-72	12.7	870	150	6-7	72-4
60 Purecal U	13 " " "	2530	475	6-7	61-3	15.5	960	425	25	55-60
" (M_n 15,600)	15 " " "	2125	450	3-4	62-3	13.0	1200	475	25	59-62
" (M_n 15,700)	15 " " "	1885	450	0	55-9	13.8	1180	425	25	60-3
"	17 " " "	1580	375	3-4	66-9	11.5	1200	400	18-9	58-62
"	19 " " "	1040	275	6-7	62-4	12.4	850	275	6-7	62-4
60 Furnex	17 " " "	2230	125	6-7	85-7	8.9	1030	125	18-9	77-9
"	19 " " "	2500	100	0-1	78-80	3.8	1075	125	1-2	65-8
60 Philblack A (M_n 15,600)	17 " " "	2400	125	0-1	82-5	7.2	940	125	6-7	68-71
" (M_n 15,700)	17 " " "	1750	100	0-1	76-9	13.2	710	100	11-2	75-8
75 Furnex	20 " " "	2495	75	0-1	84-7	4.2	960	100	3-4	67-70
"	22 " " "	2420	75	0-1	85-7	2.8	1065	75	3-4	72-4
75 Philblack A	22 DI-CUP 40C	2400	75	0-1	89-92	4.6	750	75	6-7	78-80
30 Philblack A + 30 Purecal U	12 " " "	2210	225	0-1	69	4	1140	225	7-8	62-4
"	14 " " "	2210	200	0-1	70	5	1300	200	7-8	62-4
"	16 " " "	2270	175	0-1	73	8	1115	225	7-8	64
40 Philblack A + 20 Purecal U	14 " " "	2300	200	0-1	72	3	1580	275	7-8	62
"	16 " " "	2150	125	0-1	75-6	6	1180	175	6-7	64
50 Philblack A + 10 Purecal U	15 " " "	2260	125	0-1	80	6	1230	175	6-7	64-5
"	17 " " "	2660	125	0-1	80	4	1310	150	6-7	69

(1)

ged Properties; Plexol 201 350°F, 70 hours immersion				Aged Properties: Air at 400°F 70 Hours					Aged Properties: Air at 400°F 168 Hours				
nsile psi)	Elongation (%)	Set at Break (%)	Hardness (Shore A)	% Wt Loss	Tensile (psi)	Elongation (%)	Set at Break (%)	Hardness (Shore A)	% Wt Loss	Tensile (psi)	Elongation (%)	Set at Break (%)	Hardness (Shore A)
1335	150	3-4	67-8	6.0	1130	175	6-7	73-6	9.0	940	150	9-10	75-6
1000	75	1-2	71-3	6.4	1270	125	2-3	80-2	9.7	1200	100	6-7	83-4
1040	100	6-7	76-8	6.5	1320	100	6-7	85-7	10.2	1140	75	12-3	90-4
1000	100	3-4	77-9	6.9	1400	75	6-7	88-90	10.6	1215	75	6-7	94
1335	150	6-7	65-8	5.1	1250	150	8-9	76-8	7.7	760	150	12-3	78-80
870	150	6-7	72-4	4.6	1080	175	12-3	72-4	10.1	890	175	18-9	79-81
960	425	25	55-60	10.1	400	475	18-9	50-4	15.5	395	350	12-3	51
1200	475	25	59-62	10.0	435	450	18-9	50-4	15.4	400	300	12-3	48-50
1180	425	25	60-3	11.1	735	350	12-3	55	16.8	575	275	6-7	57-9
1200	400	18-9	58-62	11.6	975	400	18-9	56-9	15.1	910	275	9-10	60-2
850	275	6-7	62-4	12.7	885	325	9-10	58-61	16.0	695	200	3-4	60-3
1030	125	18-9	77-9	6.0	1030	75	12-3	90-3	9.6	960	25	12-3	92-4
1075	125	1-2	65-8	5.5	1085	175	3-4	62-6	7.3	895	150	3-4	67-70
940	125	6-7	68-71	5.9	1080	125	6-7	82-4	8.6	860	90	12-3	85-7
710	100	11-2	75-8	7.0	960	125	12-3	82-4	10.0	960	75	12-3	87-9
960	100	3-4	67-70	5.1	900	100	3-4	78-81	7.4	815	75	4-5	81-3
1065	75	3-4	72-4	4.3	850	75	3-4	80-3	7.3	850	75	3-4	83-6
750	75	6-7	78-80	5.7	1025	50	6-7	93	9.2	1070	50	9-10	94
1140	225	7-8	62-4	6	700	300	18-9	58-62	10	540	350	50	63
1300	200	7-8	62-4	6	900	275	12-3	63-5	11	770	275	37	67
1115	225	7-8	64	7	885	275	12-3	62-5	12	785	275	37	69-71
1580	275	7-8	62	6	780	275	6-7	57-9	10	565	275	12	56
1180	175	6-7	64	7	920	225	13-4	68	11	740	200	25	75
1230	175	6-7	64-5	5	960	200	13-4	73	8	650	175	37	75-6
1310	150	6-7	69	6	915	150	12-3	75	9	800	150	18	78

(2)

IV. EXPERIMENTAL

A. SYNTHESIS OF STARTING MATERIALS

Research on the preparation of certain novel or unusual fluorine-containing intermediates considered desirable for polymerization in this project was performed at Purdue Research Foundation under subcontract to Hooker Electrochemical Company and details of that synthetic work comprise Appendix I of this report. The materials described below were prepared at Hooker Electrochemical Company laboratories, and further details of known compounds may be found in the references cited.

Perfluoroglutaric Acid was prepared by aqueous permanganate oxidation of 1,2-dichlorohexafluorocyclopentene (Hooker Electrochemical Company) according to the method described by McBee, Wiseman, and Bachmann[2]. Yield of white crystalline perfluoroglutaric acid, purified by vacuum distillation ranged around 63%; b.p. 121-126°C/1.4-1.8 mm.

Diethyl Perfluoroglutarate[2] was prepared by refluxing a mixture of perfluoroglutaric acid and 100% excess ethanol with a small amount of sodium bisulfate in benzene, as described previously[1b]. When purified perfluoroglutaric acid, as above, was used, yield of the colorless ester after sodium bicarbonate and water washes, drying, and distillation was 85%; b.p. 57°C/0.6 mm. When crude perfluoroglutaric acid was used, yield of colorless ester after washes, drying and two distillations was 50%; b.p. 54-55°C/0.6 mm.

2,2,3,3,4,4-Hexafluoropentanediol was prepared by reduction of diethyl perfluoroglutarate with lithium aluminum hydride (Metal Hydride, Inc.) according to the method reported by McBee, Marzluff, and Pierce[3]. Yield of white crystalline diol was 93% after three recrystallizations from benzene; m.p. 77-78.5°C.

Perfluoroadipic Acid[2], Diethyl Perfluoroadipate[2], and 2,2,3,3,4,4,5,5-Octafluorohexanediol[3] were prepared in a manner similar to that outlined above for the perfluoroglutarate series, and as also prepared previously[1b]. Yields in this series of reactions were slightly lower than in the corresponding series described above.

2,2,3,3,4,4-Hexafluoropentane-1,5-bis(p-toluenesulfonate) was synthesized from the fluorine-containing diol and p-toluenesulfonyl chloride in a manner similar to that used by Tiers, Brown, and Reid[9] to prepare monotosylate esters from fluorine-containing alcohols.

A mixture of 106 g. (0.5 mole) of 2,2,3,3,4,4-hexafluoropentanediol, 200 g. (1.05 mole) p-toluenesulfonyl chloride, and 225 ml of water was stirred and heated to 40°C while 40 g. (1 mole) sodium hydroxide in 160 ml of water was added over a one and one-half hour interval. After two hours, the mixture was still basic, and 100 ml of dioxane was added. The mixture was allowed to stand over a week-end.

A white precipitate was collected in two fractions and was washed with conc. ammonium hydroxide. Recrystallization of the lower melting fraction (m.p. 84-86°C) from methylene chloride raised its melting point to that of the other fraction collected (m.p. 92-94°C). Yield of crude ditosylate was 170 g. (65%) m.p. 92-94°C.

An analytical sample of 2,2,3,3,4,4-hexafluoropentane-1,5-bis(p-toluenesulfonate) was recrystallized four times from ethanol; m.p. 95-96°C.

Anal. Calcd. for $C_{19}H_{18}O_6F_6S_2$: C, 43.85; H, 3.46; F, 21.92; S, 12.31.

Found: C, 44.00; H, 3.26; F, 22.00; S, 12.17.

The melting point of this ditosylate reported earlier in Appendix I of reference 1a is in error.

2,2,3,3,4,4-Hexafluoropentane-1-ol-5-p-toluenesulfonate was isolated by evaporation of the methylene chloride solution, above. The remaining oily solid was vacuum distilled to give a viscous oil, b.p. 185°C/1.3 mm, and a small amount of white solid, m.p. 95-110°C. The oil was filtered and redistilled twice, the main fraction being pure 2,2,3,3,4,4-hexafluoropentane-1-ol-5-p-toluenesulfonate; b.p. 150-151°C/0.1 mm; n_D^{29} = 1.4629.

Anal. Calcd. for $C_{12}H_{12}O_4F_6S$: C, 39.36; H, 3.28; F, 31.19; S, 8.75.

Found: C, 39.56; H, 3.32; F, 31.37; S, 8.73.

A compound melting at 94.5°-95.5°C was reported earlier in Appendix I of reference 1a, erroneously, to be the mono-tosyl ester of 2,2,3,3,4,4-hexafluoropentanediol. This was actually the ditosylate, as shown above.

Bis(N-methyl)perfluoroglutaramide was synthesized from the reaction of methylamine with an ethereal solution of 226 g. (1 mole) diethyl perfluoroglutarate. The reaction was stopped several times to filter off product and to remove precipitate from the gas inlet tube. Methylamine was led into the reaction mixture until no further precipitate formed. Yield of crude diamide after recrystallization from benzene was 186 g. (70%); m.p. 143-144°C.

An analytical sample of bis(N-methyl)perfluoroglutaramide was recrystallized three times from benzene; m.p. 144-144.5°C.

Anal. Calcd. for $C_7H_8O_2F_6N_2$: C, 31.6; H, 3.01; F, 42.85; N, 10.5.

Found: C, 31.85; H, 3.28; F, 43.06; N, 10.67.

N-Methyl-4-carboethoxyperfluorobutyramide was isolated by evaporation of the benzene solution, above. An oily residue was obtained which was added to methanol and water, and separated and dried. Distillation gave 25 g. (9%) of colorless N-methyl-4-carboethoxyperfluorobutyramide; b.p. 94-95°C/

0.65 mm; $n_D^{29} = 1.3803$.

Anal. Calcd. for $C_8H_9O_3F_6N$: C, 34.18; H, 3.20; F, 40.58; N, 4.98.

Found: C, 34.23; H, 3.05; F, 40.73; N, 5.15.

Reaction of 2,2,3,3,4,4-hexafluoropentane-1,5-bis(p-toluenesulfonate) with methylamine was tried at 130°C and at 165°C. At the higher temperature some reaction occurred and the resultant mixture was extracted with dioxane, ether and benzene. The residue was dissolved in chloroform. From these fractions a yield of 14% of N-methyl-p-toluenesulfonamide, m.p. 77.5-79°C has been separated and identified by mixed melting point and infra-red spectra. A solid melting at 146.5-147.5°C which contained nitrogen and sulfur was also isolated in about 20% yield. The solid has not yet been further characterized.

Hydrogenation of bis(N-methyl)perfluoroglutaramide was run at 175°C in the presence of methylamine, initial hydrogen pressure of 2500 psi, with 11% of mixed catalyst containing Harshaw catalyst Cu 1106 (copper chromite with 10% BaO) and a small amount of Raney nickel. At 125°C, bomb pressure was 3150 psi and remained constant through continued temperature rise to 175°C. Total heating time was 5 hours, 1.5 hours at 175°C. The reaction mixture was washed out with methanol and filtered. Starting material was recovered by crystallization from methanol-benzene; mixed melting point with bis(N-methyl)perfluoroglutaramide gave no depression. Evaporation of the solvent gave a dark oil, which after two distillations gave a colorless liquid; b.p. 53°C/1.6 mm. On cooling, the liquid crystallized; it melted at around room temperature. Infra-red spectra showed a new NH function, increased CH_2 frequency, and the presence of an amide group, indicating that the low-melting solid may be the mono-reduction product of bis(N-methyl)perfluoroglutaramide.

Reaction of 2,2,3,3,4,4-hexafluoropentanediol with aniline in the presence of Raney nickel was attempted in a manner similar to that reported for the reactions of hydrocarbon alcohols and amines[4-7]. A small amount of sodium was added to the reaction mixture in order to form catalytic amounts of the mono-sodium salt of the diol. While the mixture was being heated some hydrogen and a small amount of water were given off, indicating that the first steps in the reaction sequence may have occurred, at least on one end of the diol. Starting material and a small amount of yellow oil, b.p. 100°C/2.5 mm were isolated from the reaction mixture. Interpretation of infra-red spectra of the oil appears to be consistent with the structure $HOCH_2(CF_2)_3CH = NC_6H_5$.

Suberyl and Azelayl Chlorides were prepared from equivalent amounts of the corresponding acids and phosphorus pentachloride in the usual manner. Yields were generally good (up to 87%), although decomposition during distillation sometimes occurs. Suberyl chloride boiled at 122-123°C/2.9 mm; azelayl chloride boiled at 124-127°C/2.2-2.5 mm.

Other hydrocarbon materials used in the preparation of polyesters reported in Section B of this report were prepared or were purchased as described previously[1b]. All substances used were carefully purified by either redistillations or recrystallizations.

B. POLYMERS

The methods and techniques employed in the preparation and characterization of the linear polyesters have been described previously[1], except that a small amount of high boiling liquid, either o-dichlorobenzene or dichlorohexafluoroxylene (depending on the solubility of the polymer) was incorporated in the reaction mixture.

Viscometer tubes and methods described by Flory[8] for the determination of melt viscosities (η) and molecular weights (M_n), etc., of hydrocarbon polyesters were applied in this work to the fluorine-containing polyesters.

Hexafluoropentylene adipate was extremely well suited for processing on conventional rubber equipment. Milling in the specified amounts of reinforcing agent, followed by antioxidant (when used) and curing agent (DI-CUP 40C), was accomplished on water-cooled or on slightly-warmed rollers, depending on the molecular weight (M_n) of the gum rubber.

Cure with DI-CUP 40C (a mixture containing 40% dicumyl peroxide on calcium carbonate) was standardized at 160°C for 50 minutes in stainless steel molds with platen pressures of about 20,000 pounds for the 4" x 4" x 0.025" mold.

Testing of dumbbell specimens cut from the moldings were performed in the usual way, as described previously[1b]. The tests were conducted on 0.025" thick dumbbell specimens except for the low temperature tests performed at B F Goodrich Company which were run on 0.075" thick specimens.

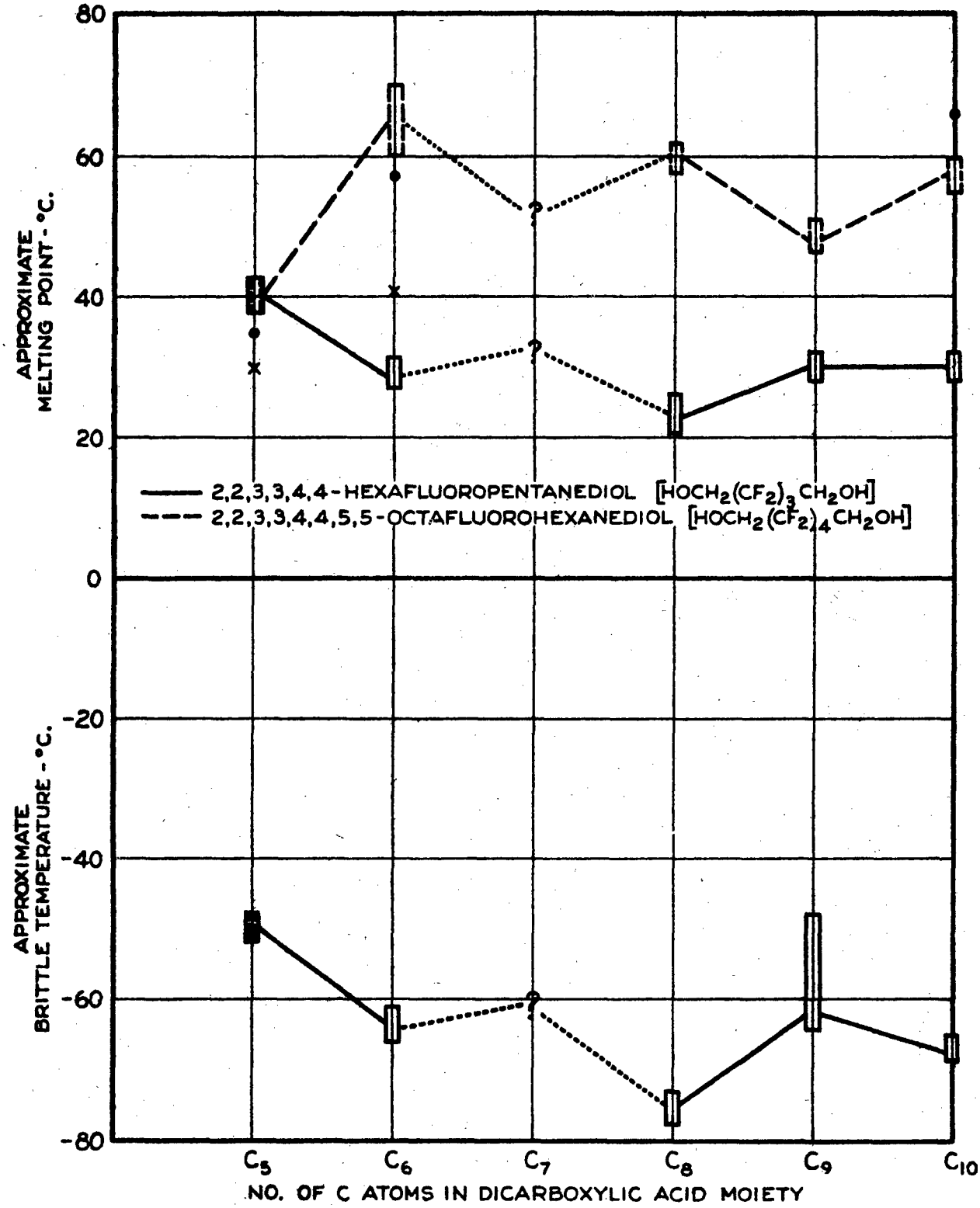

FIGURE 1

MELTING AND BRITTLE TEMPERATURES FOR FLUORINE-CONTAINING POLYESTERS

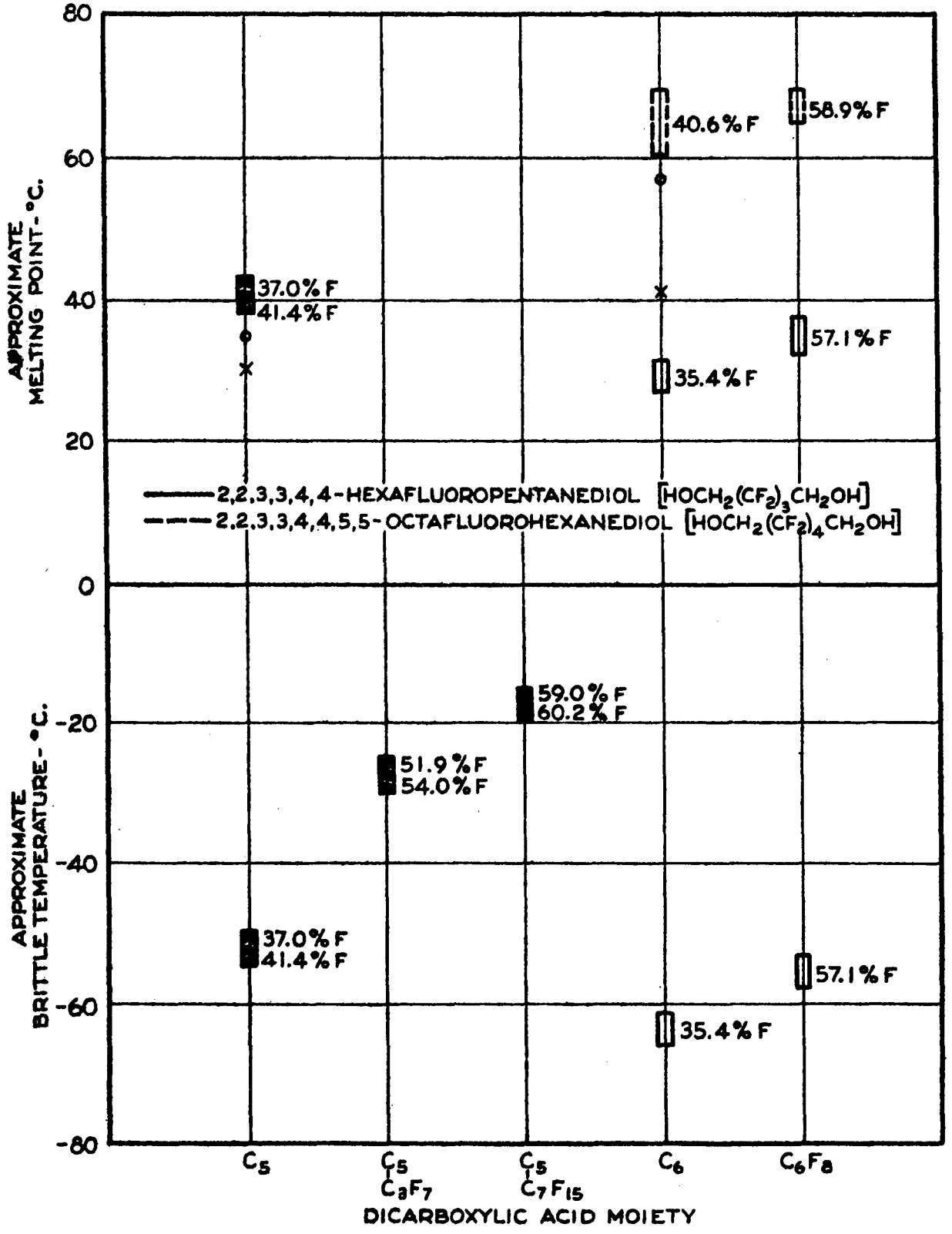

FIGURE 2

EFFECT OF FLUORINE CONTENT AND POSITION ON MELTING AND BRITTLE TEMPERATURES

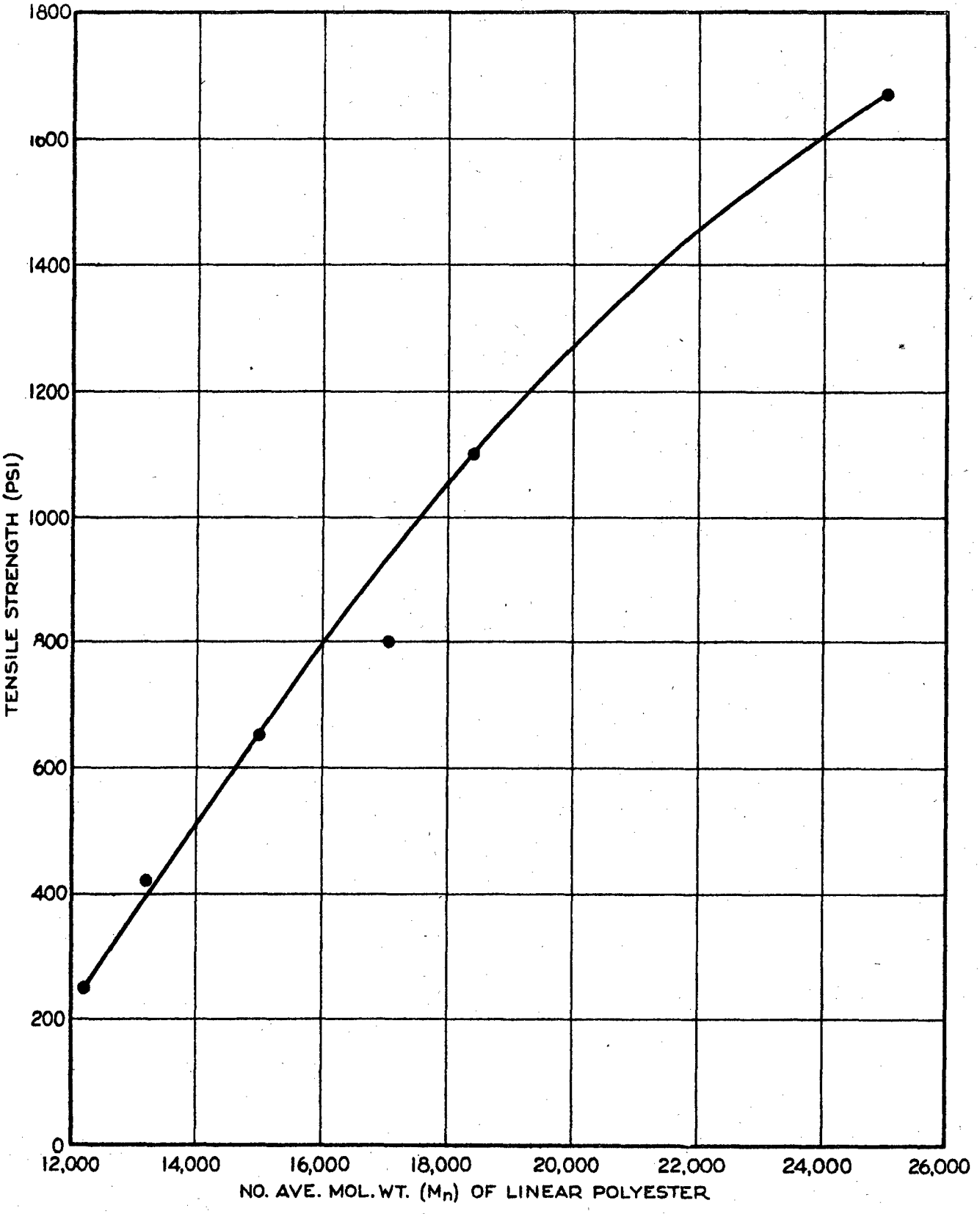

FIGURE 3

TENSILE STRENGTH VS MOLECULAR WEIGHT OF HEXAFLUOROPENTYLENE ADIPATE GUM VULCANIZATES

GEHMAN LOW TEMPERATURE TORSION
TEST OBTAINED FROM A.E.JUVE, DIRECTOR,
TECHNICAL SERVICE RESEARCH,
B.F. GOODRICH CO.

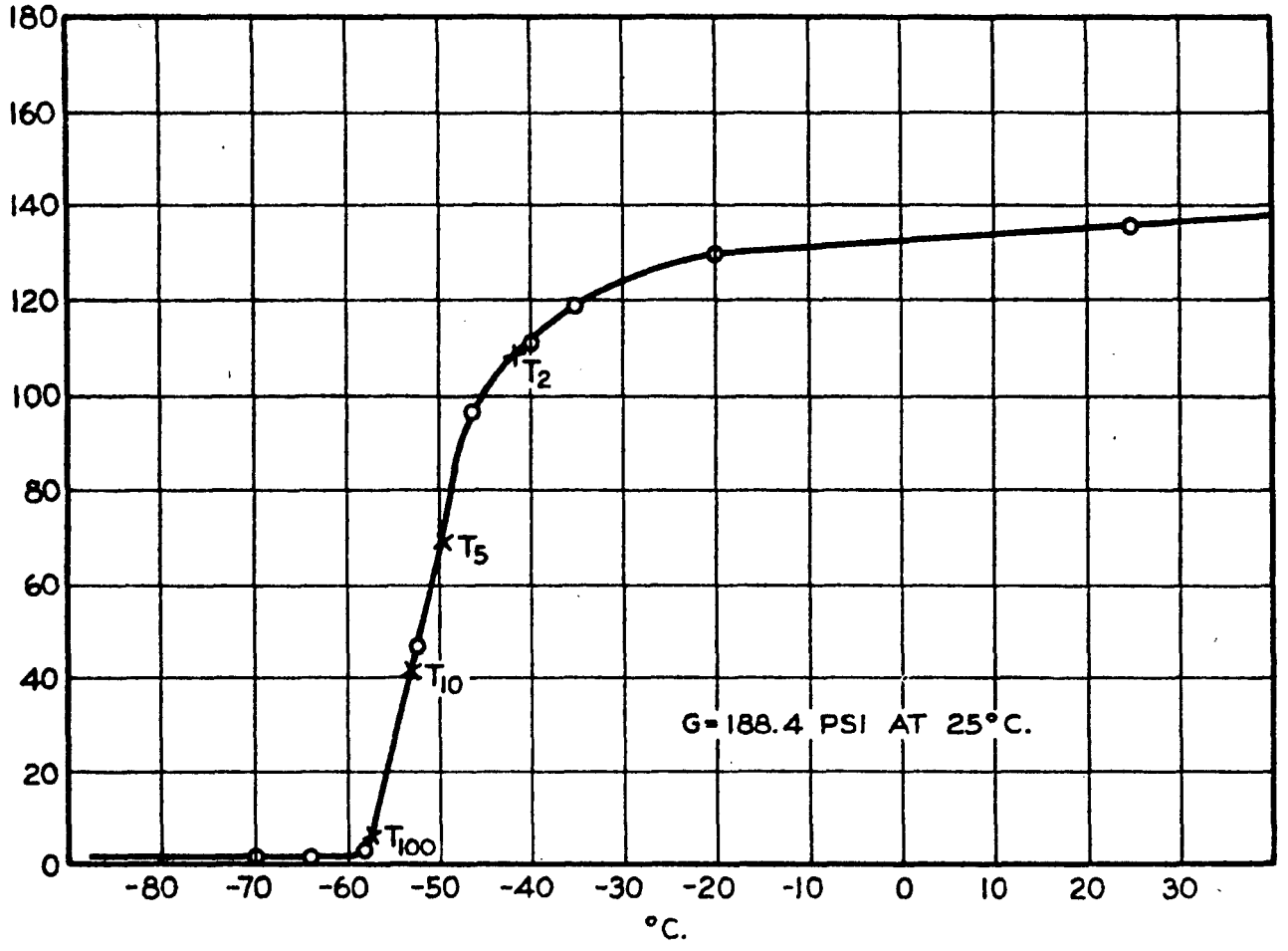

FIGURE 4

LOW TEMPERATURE FLEXIBILITY OF HEXAFLUOROPENTYLENE ADIPATE CARBON BLACK REINFORCED VULCANIZATES

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APPENDIX I

SUBCONTRACT WORK PERFORMED AT PURDUE UNIVERSITY

Research on the synthesis of certain difunctional compounds containing fluorine, or fluorine in combination with hetero atoms interspersed in the carbon chain, such as sulfur, oxygen, and nitrogen, has been performed at the Department of Chemistry and Purdue Research Foundation, Purdue University, under subcontract to Hooker Electrochemical Company. In general, novel fluorocarbon compounds considered desirable as starting materials for polymer reactions for this project, at the present stage, consist of dicarboxylic acids from which the corresponding dicarboxylic acid chlorides can be made. It was considered important to investigate the effects produced on the polymers after polymerization of compounds such as those containing fluorine on pendent groups attached to the linear chain as well as those containing fluorine directly on the linear chain, but not alpha or beta to the carbonyl function.

This appendix comprises the summary report of the research performed at Purdue University under subcontract to Hooker Electrochemical Company during the 1956 contract year.

Summary Progress Report

FLUORINE CONTAINING MONOMERS FOR CONDENSATION POLYMERS

Earl T. McBee

Department of Chemistry and the Purdue Research Foundation
Purdue University

1 December 1955 to 1 November 1956

Subcontract with the
Hooker Electrochemical Company
Niagara Falls, New York

on

Contract AF 33(616)-2421
Project No. 7340

FOREWORD

This summary progess report was prepared by the Department of Chemistry, Purdue University on work concerned with the investigation and development of new fluorine-containing monomers suitable for condensation type polymers. This work was performed on a subcontract with the Hooker Electrochemical Company as part of Contract AF 33(616)-2421, Project No. 7340, "Rubber, Plastic, and Composite Materials", Task Number 73404, "Synthesis and Evaluation of New Polymers".

The personnel assigned to this project were Mr. Gordon Wilson, Jr. and Mr. Leslie David Moore under the direct supervision of Dr. E.T. McBee. Dr. Carleton W Roberts served as co-director during the period 1 December 1955 to 31 July 1956.

ABSTRACT

A. SULFUR-CONTAINING MONOMERS

1. The addition of ethyl mercaptoacetate to ethyl 4,4,5,5,6,6,6-heptafluoro-2-hexenoate gave diethyl 3-perfluoropropyl-4-thiaädipate in 85% yield.

2. The hydrolysis of diethyl 3-perfluoropropyl-4-thiaädipate with formic acid produces the corresponding thiaädipic acid in good yield.

B. OXYGEN-CONTAINING MONOMERS

1. The reaction of ethyl 4,4,5,5,6,6,6-heptafluoro-2-hexenoate with ethyl 3-hydroxy-4,4,5,5,6,6,6-heptafluorohexanoate in the presence of sodium hydride has been reinvestigated.

2. The reaction of ethanol with ethyl 4,4,5,5,6,6,6-heptafluoro-2-hexenoate in the presence of sodium ethoxide led to ethyl 3-ethoxy-4,4,5,5,6,6,6-heptafluorohexanoate.

3. The addition of hydrogen bromide to ethyl 4,4,5,5,6,6,6-heptafluoro-2-hexenoate has been attempted.

C. NITROGEN-CONTAINING MONOMERS

1. The addition of methylamine to ethyl 4,4,5,5,6,6,6-heptafluoro-2-hexenoate yields ethyl 3-methylamino-4,4,5,5,6,6,6-heptafluorohexanoate.

2. The addition of ethyl 3-methylamino-4,4,5,5,6,6,6-heptafluorohexanoate to ethyl 4,4,5,5,6,6,6-heptafluoro-2-hexenoate has been investigated.

3. The preparation of ethyl 3-carbethoxymethylmethylamino-4,4,5,5,6,6,6-heptafluorohexanoate from ethyl 3-methylamino-4,4,5,5,6,6,6-heptafluorohexanoate and ethyl bromoacetate has been attempted.

D. MONOMERS CONTAINING FLUORINE IN THE BACKBONE

1. The cyanoethylation of 2,2,3,3,4,4-hexafluoro-1,5-pentanediol gives a mixture of mono- and di-cyanoethylation products.

2. Attempts to hydrolyze the di-cyanoethylation product obtained from 2,2,3,3,4,4-hexafluoro-1,5-pentanediol were made.

3. Sodium hydride has been used in an attempt to prepare 1,5-bis-carbethoxymethoxy)-2,2,3,3,4,4-hexafluoropentane from hexafluoro-1,5-pentane diol and ethyl bromoacetate.

4. The addition of 2,2,3,3,4,4-hexafluoro-1,5-pentanediol to methyl acrylate has been investigated.

5. 1,5-bis(Carboxymethyoxy)-2,2,3,3,4,4-hexafluoropentane has been prepared by hydrolysis of the corresponding ester.

6. Diethyl perfluoroglutarate has been reduced to perfluoropentanedial.

7. An initial investigation of the reaction of perfluoropentanedial with malonic acid has been performed.

8. The reaction of diethyl perfluoroglutarate with a mixture of methylmagnesium iodide and isopropylmagnesium bromide gave a small amount of 3,3,4,4,5,5-hexafluoro-2,6-heptanediol.

E. REPEATED PREPARATIONS

1. Ethyl 4,4,5,5,6,6,6-heptafluoro-2-hexenoate was prepared from perfluorobutyric acid by esterification, reduction to the aldehyde, condensation with malonic acid, esterification of the resulting β-hydroxy acid and finally dehydration with phosphorous pentoxide.

2. 3-Hydroxy-4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-pentadecafluorodecanoic acid, the corresponding ethyl ester and the α,β-unsaturated ester; 3,5-bis(perfluoropropyl)-4-thiapimelyl chloride; ethyl 3-mercapto-4,4,5,5,6,6,6-heptafluorohexanoate and 3-perfluoropropylglutaric anhydride have been prepared in order to obtain ultimate analyses.

SUMMARY AND CONCLUSIONS

A major portion of this contract period has been spent in repeated synthesis and development of new syntheses for the preparation of fluorine-containing difunctional monomers.

The 3-perfluoroalkylglutaric acid series of compounds has been completed. Further work has been done on the perfluoropropyl substituted thia-, aza- and oxa-substituted pimelic and adipic acids.

Major new efforts have been directed at the synthesis of diacids and diols having fluorine in the backbone. This aspect of the investigation is most promising and it is planned to continue major future efforts along these routes during the next contract period. In particular satisfactory methods are being developed for compounds of the following general structure:

1. $HOOCCH_2CH_2(CF_2)_3CH_2CH_2COOH$
2. $HOCH_2CH_2CH_2(CF_2)_3CH_2CH_2CH_2OH$
3. $HOOCCH_2OCH_2(CF_2)_3CH_2OCH_2COOH$
4. $HOCH_2CH_2OCH_2(CF_2)_3CH_2OCH_2CH_2OH$
5. $HOOCCF_2SCF_2COOH$

DISCUSSION

A. SULFUR-CONTAINING MONOMERS

Ethyl mercaptoacetate has been added to ethyl 4,4,5,5,6,6,6-heptafluoro-2-hexenoate in the presence of piperidine and Triton B to give diethyl 3-perfluoropropyl-4-thiaadipate in 67% yield. This reaction was repeated using larger quantities and the yield has been increased to 85%. Hydrolysis to the corresponding thiaadipic acid under the same conditions used for hydrolysis of diethyl 3,5-bis-(perfluoropropyl)-4-thiapimelate gave only a low yield of the acid. Other products were yellow oils which were acidic and could be mixtures of unreacted diester and mono-acid. Since the yield of the thiaadipic acid was only 21% another method of hydrolysis was sought. When the thiaadipic ester was hydrolyzed by ester interchange using formic acid the yield of thiaadipic acid was 82%.

B. OXYGEN-CONTAINING MONOMERS

The reaction of ethyl 3-hydroxy-4,4,5,5,6,6,6-heptafluorohexanoate with ethyl 4,4,5,5,6,6,6-heptafluoro-2-hexenoate in the presence of sodium hydride was reported previously[1]. At that time the main product which was isolated could not be identified. The reaction has been reinvestigated during this period. Sodium hydride was added to a solution of the α,β-unsaturated ester and the hydroxy compound. Since the sodium salt of the β-hydroxy ester was not soluble in the non-polar benzene, ethyl alcohol was added to obtain a homogeneous phase. After heating to reflux for three hours followed by acidification and removal of the solvents the same liquid product was obtained that had previously been isolated. This substance proved to be ethyl 3-ethoxy 4,4,5,5,6,6,6-heptafluorohexanoate which arose from the addition of ethyl alcohol to the α,β-unsaturated ester. It has also been prepared in the absence of the β-hydroxyheptafluorohexanoate.

A further attempt has been made to react the sodium salt of ethyl 3-hydroxy-4,4,5,5,6,6,6-heptafluorohexanoate with ethyl 4,4,5,5,6,6,6-heptafluoro-2-hexenoate. In this preparation, an acidic substance is added to react with any unreacted sodium hydride before the isolation of products is attempted. Since when ethanol was used for this purpose ethyl 3-ethoxy-4,4,5,5,6,6,6-heptafluorohexanoate resulted, water in dioxane was added to the cooled reaction mixture and the only compounds isolated were the two starting materials (β-hydroxy- and α,β-unsaturated esters) and the free acids corresponding to the starting materials.

Since the addition of the β-hydroxy ester to the α,β-unsaturated ester does not appear to be easily accomplished an alternate synthesis has been sought. A Williamson ether synthesis with the β-bromo ester and the salt of the β-hydroxy ester is to be investigated. Toward this end, the addition of hydrogen bromide to ethyl 4,4,5,5,6,6,6-heptafluoro-2-hexenoate has been undertaken. Using the method of Walborsky and Schwarz[2] a very small amount of an impure ester containing bromine and fluorine has been isolated, but in poor yield.

C. NITROGEN-CONTAINING MONOMERS

The preparation of the nitrogen analogs of the 4-thiapimelate and 4-thiaadipate has been attempted. The addition of one mole of methyl amine to two moles of ethyl 4,4,5,5,6,6,6-heptafluoro-2-hexenoate at 100°C gave only the 1:1 adduct. Even when this secondary amine was heated at 175°C with the α,β-unsaturated ester the tertiary amine was not formed. The reaction of ethyl 3-methylamino-4,4,5,5,6,6,6-heptafluorohexanoate with ethyl bromoacetate in the presence of anhydrous potassium carbonate was also unsuccessful.

D. MONOMERS CONTAINING FLUORINE IN THE BACKBONE

1. Cyanoethylation of Hexafluoro-1,5-pentanediol

Initial investigation of the cyanoethylation of 2,2,3,3,4,4-hexafluoro-1,5-pentanediol has been started. When acrylonitrile and the diol, along with a catalytic amount of Triton B, were refluxed in ethyl ether there was very little if any reaction. This is surprising since most primary and secondary alcohols easily add to acrylonitrile at low temperatures[3]. Also, the hydroxyl hydrogens of the diol should be easily lost due to the inductive effect of the fluorines[4], thus promoting the reaction. The reaction was repeated using dioxane as the solvent. Besides unreacted diol, two products were isolated. The lower-boiling substance has in infra-red spectrum that indicates the presence of a hydroxyl as well as a nitrile function and is thus assumed to be the mono-cyanoethylation product, 5-cyanoethoxy-2,2,3,3,4,4-hexafluoro-pentanol. The higher-boiling substance shows only the presence of the nitrile function in its infra-red spectrum and is believed to be the di-cyanoethylation product, 1,5-bis(2-cyanoethoxy)-2,2,3,3,4,4-hexafluoropentane.

Attempts to hydrolyze the di-cyanoethylation product have not met with success. The compound gives the original hexafluoropentanediol when subjected to basic hydrolysis conditions. When heated with concentrated hydrochloric acid a very small amount of the same diol was obtained along with black oil and tar. Similar results, that is, the cleavage of the ether linkage, have been observed for the attempted hydrolysis of 1,4-bis(2-cyano-ethoxy)-pentane[5]. With aqueous sulfuric acid, the reaction product was again the hexafluoropentanediol. However, side reactions leading to tars and highly colored products which were encountered in previous hydrolyses were minimized in this hydrolysis and the diol was obtained in 78% yield.

The cyanoethylation reaction discussed above is one synthetic route to 1,5-bis(2-carboxyethoxy)-2,2,3,3,4,4-hexafluoropentane. Another preparation of the diacid-diether might be by way of a Williamson ether synthesis using a β-halopropionate and the di-sodium salt of hexafluoropentanediol. An investigation of this alternate synthesis has been started. Since there was no β-halopropionate available the reaction between the salt of the diol and ethyl bromoacetate was attempted. Difficulty was encountered in obtaining complete solution of the metallic sodium in a solution of the diol in dioxane. However, with the majority of the sodium dissolved, ethyl bromoacetate was added and the reaction mixture refluxed for several hours. A

high-boiling neutral liquid was isolated from this reaction mixture. Ultimate analysis of this product substantiates the belief that it is the desired 1,5-bis(carbethoxymethoxy)-2,2,3,3,4,4-hexafluoropentane. The product has been hydrolyzed with formic acid to produce the corresponding 1,5-bis(carboxymethoxy)-2,2,3,3,4,4-hexafluoropentane. An attempt to prepare the diether-diester using sodium hydride instead of metallic sodium was made. The hydride and diol were refluxed together in dioxane for 24 hours before adding ethyl bromoacetate. The hydride supposedly does not react with alkyl halides so even though there was not complete solution of the hydride when the acetate was added, the remaining hydride should have reacted as the sodium salt of the diol was converted to the ether. Although the reaction mixture was refluxed for 39 hours there was very little sodium bromide formed and a 62% recovery of diol was realized along with a quantity of red tar.

The hydrolysis of the product obtained by cyanoethylation of 2,2,3,3,4,4-hexafluoro-1,5-pentanediol results in cleavage of the ether linkage; however, the diester-diether 1,5-bis(carbethoxymethoxy)-2,2,3,3,4,4-hexafluoropentane was easily hydrolyzed by ester interchange using formic acid. Thus, if the diester corresponding to the cyanoethylation product could be prepared it should be possible to hydrolyze it with formic acid. Therefore, 2,2,3,3,4,4-hexafluoro-1,5-pentanediol was reacted with methyl acrylate using the sodium salt of the diol as catalyst. As has been found in other reactions of this diol, the reaction appears to go sluggishly and stop far from completion. When the reactants were dissolved in dioxane, allowed to stand overnight and then refluxed for one hour there was apparently little reaction since 91% of the diol was recovered when the acidified reaction mixture was distilled. With a longer reflux period the recovery of diol was 32% and a high boiling liquid product was isolated. If this substance, which contains fluorine and appears to be an ester, is the desired diester-diether the yield amounts to 43%. A slightly altered procedure on another run gave 31% recovery of diol and 49% of the impure liquid product.

2. Reactions of Perfluoropentanedial

The reduction of diethyl perfluoroglutarate to the corresponding dialdehyde has been investigated. The dialdehyde appears to form a fairly stable hydrate which is only partially decomposed when the reaction product is distilled. The dialdehyde also polymerizes readily. The reaction of perfluorobutyraldehyde with malonic acid in the presence of pyridine goes in good yield even when the partially hydrated aldehyde is used. Also, when the pyridine solution of malonic acid is added to the aldehyde it polymerizes rapidly. Therefore, it was thought possible to react the partially hydrated and polymerized perfluoropentanedial under the same conditions and obtain a long chain dicarboxylic acid containing fluorine in the backbone of the molecule. Dehydration followed by hydrogenation should yield a saturated compound suitable for use in the preparation of polyesters. Toward this end, a sample of the dialdehyde was prepared.

Attempts to react this dial with malonic acid in the presence of base have been unsuccessful.

E. REPEATED PREPARATIONS

A considerable portion of this contract period has been spent in preparing compounds which have already been described. A large quantity of ethyl 4,4,5,5,6,6,6-heptafluoro-2-hexenoate was desired for further investigations and thus many of the reactions which have been run are on the synthetic route to this ester. Five moles of perfluorobutyric acid were esterified with ethyl alcohol in each of two runs. The combined crude ethyl perfluorobutyrate was distilled to yield 9.2 moles (92%) of pure ester. The ester was reduced at -70°C. with lithium aluminum hydride in two four-mole batches to give perfluorobutyraldehyde in 72% and 76% yield.

Since the Reformatsky procedure is difficult and gives inconsistent yields, a Knoevenagle condensation of perfluorobutyraldehyde with malonic acid in the presence of pyridine was conducted. The resulting β-hydroxy acid was esterified and dehydrated to give the α,β-unsaturated ester.

In a similar manner, ethyl 4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-pentadecafluoro-2-decenoate was prepared starting with perfluorooctanoic acid.

Several other compounds were prepared again in order to obtain acceptable carbon and hydrogen analyses.

EXPERIMENTAL

A. SULFUR-CONTAINING MONOMERS

1. Preparation of Diethyl 3-Perfluoropropyl-4-thiaadipate. A solution of 80.4 grams (0.30 mole) of ethyl 4,4,5,5,6,6,6-heptafluoro-2-hexenoate in 150 ml of absolute ether was placed into a 1000 ml three-neck flask fitted with a stirrer, condenser and addition funnel. After adding 5 ml each of Triton B and piperidine, a solution of 36.0 grams (0.30 mole) ethyl mercaptoacetate in 50 ml of absolute ether was added slowly. The heterogeneous mixture was stirred at room temperature for 18 hours, then refluxed for 2 hours and finally poured into 100 ml of cold water. The ether layer was removed and the water layer was extracted with two 75 ml portions of ether. The combined ether solutions were washed with 50 ml of each of 10% sulfuric acid, 10% sodium carbonate and water. The dried (over magnesium sulfate) ether solution yielded upon distillation 99.5 grams (85%) of diethyl 3-perfluoropropyl-4-thiaadipate, b.p. 85°C (0.4 mm), n_D^{20} 1.4028.

Anal. Calculated for $C_{12}H_{15}F_7O_4S$: C, 37.11; H, 3.89.

Found: C, 37.18; H, 3.73.

2. Preparation of 3-Perfluoropropyl-4-thiaadipic Acid. A three-neck flask of 200 ml capacity was fitted with a thermometer, stirrer and 25 cm Vigreux column connected to a total reflux head. Into the flask were placed 38.8 grams (0.1 mole) of diethyl 3-perfluoropropyl-4-thiaadipate and 24.5 grams (0.4 mole) 90% aqueous formic acid. The reaction mixture was stirred and heated at 105-110°C. Over a 48-hour period approximately 25 ml of distillate was removed, b.p. 51-70°C. The hot reaction mixture was then poured into 200 ml of ice and water and the aqueous solution was extracted with three 100 ml portions of 10% sodium carbonate solution. The carbonate solutions were acidified with concentrated sulfuric acid and extracted with three 75 ml portions of ether. The ether extracts were combined, dried over magnesium sulfate and then distilled to remove the ether. The residual oil solidified on cooling and was recrystallized from 200 ml of benzene. The yield of the 3-perfluoropropyl-4-thiaadipic acid, m.p. 72-5°C, was 27.0 grams (81.5%).

Neutral Equivalent: Calculated, 166; Found, 168, 169.

B. OXYGEN-CONTAINING MONOMERS

1. Attempted Preparation of Di-(carbethoxymethyl-2,2,3,3,4,4,4-heptafluorobutyl) Ether. Into a 300 ml three-neck flask fitted with a condenser, stirrer and addition funnel were placed 100 ml of dry dioxane. The flask was swept out with dry nitrogen while being cooled in an ice bath. When approximately half the dioxane had solidified 1.2 grams (0.05 mole) of sodium hydride was added. After slowly adding 14.3 grams (0.05 mole) of ethyl 3-hydroxy-4,4,5,5,6,6,6-heptafluorohexanoate the mixture was stirred overnight at room temperature. A solution of 13.4 grams (0.05 mole) of ethyl 4,4,5,5,6,6,6-heptafluoro-2-hexenoate in 100 ml of dry dioxane was then added and the reaction

mixture slowly heated to reflux. After 10 hours of refluxing another 14.3 grams (0.05 mole) of the β-hydroxy ester was added and the mixture refluxed an additional 12 hours. To the cooled reaction mixture, a solution of 10 ml of water in 50 ml of dioxane was added to react with any unreacted sodium hydride. Most of the solvent was removed by evaporation under reduced pressure. The residue was poured into a mixture of 200 grams of ice and 5 ml of concentrated sulfuric acid. The acidic aqueous solution was extracted with three 200 ml portions of ether and the combined ether extracts were washed with two 50 ml portions of 10% sodium bicarbonate. The dried ether solution was evaporated and the residual oil distilled to yield 6.65 grams (49% recovery) of ethyl 4,4,5,5,6,6,6-heptafluoro-2-hexenoate and 12.9 grams (45% recovery) of ethyl 3-hydroxy-4,4,5,5,6,6,6-heptafluorohexanoate. The basic washings were acidified with sulfuric acid and extracted with ether. After drying and evaporating off the ether 6.0 grams of 4,4,5,5,6,6,6-heptafluoro-2-hexenoic acid was obtained by distillation, b.p. 80-91°C (10 mm). This represents a 50% recovery of the α,β-unsaturated ester. The residue from this distillation was taken up in hot benzene, decolorized with charcoal and cooled to yield 3.5 grams 3-hydroxy-4,4,5,5,6,6,6-heptafluorohexanoic acid, m.p. 74-76°C. This represents a 13.5% recovery of the β-hydroxy ester.

In an identical experiment, 95% ethyl alcohol was used to react with any unreacted sodium hydride. This led to isolation of an additional liquid product, ethyl 3-ethoxy-4,4,5,5,6,6,6-heptafluorohexanoate, b.p. 110-113°C (80 mm), n_D^{20} 1.3502-1.3520.

2. Preparation of Ethyl 3-Ethoxy-4,4,5,5,6,6,6-heptafluorohexanoate. Metallic sodium (1.15 grams, 0.05 mole) was dissolved in 100 ml of absolute ethanol and 13.4 grams (0.05 mole) of ethyl 4,4,5,5,6,6,6-heptafluoro-2-hexenoate was added. The mixture was refluxed overnight and the excess ethanol removed by distillation under reduced pressure. The resulting paste was extracted with benzene, then dissolved in water and made acidic with dilute sulfuric acid. The acidic solution was extracted with three 75 ml portions of ether and the ether extracts dried over magnesium sulfate. Distillation produced 7.6 grams of 4,4,5,5,6,6,6-heptafluoro-2-hexenoic acid, m.p. 48-49°C. The dried benzene extracts yielded 3.1 grams of a liquid product, b.p. 106-111°C (79 mm), n_D^{20} 1.3520-1.3523. Fractionation gave a sample of the pure ester, b.p. 88°C (22 mm), n_D^{20} 1.3516, d_4^{20} 1.311.

Anal. Calculated for $C_{10}H_{13}F_7O_3$: M_R 51.27 (Vogel), 52.67 (Eisenlohr); C, 38.22; H, 4.17. Found: M_R 51.69; C, 38.11; H, 4.31.

3. Attempted Addition of Hydrogen Bromide to Ethyl 4,4,5,5,6,6,6-Heptafluoro-2-hexenoate. Into a combustion tube were placed 13.4 grams (0.05 mole) of ethyl 4,4,5,5,6,6,6-heptafluoro-2-hexenoate and 30 ml of ethyl bromide. The solution was saturated with hydrogen bromide at -7°C, sealed and heated at 100°C for 10 hours. The tube was opened and the contents poured over ice. The organic matter was taken up in pentane, washed with water, dried and distilled to give 10.60 grams (79%) recovery of the

α,β -unsaturated ester, b.p. 74-75°C (71 mm), n_D^{23} 1.3438-1.3448, and 1.85 grams of a liquid, b.p. 108°C (71 mm), n_D^{23} 1.3680-1.3700, which contains bromine and fluorine and gives a positive hydroxamic acid test for an ester.

4. Cyanoethylation of 2,2,3,3,4,4-Hexafluoro-1,5-pentanediol. Into a 1-l flask were placed 63.3 grams (0.30 mole) of 2,2,3,3,4,4-hexafluoro-1,5-pentanediol, 42.4 grams (0.80 mole) of acrylonitrile, 120 ml of dioxane, 3 ml of saturated potassium hydroxide in methanol and 2 ml of triton B solution. With stirring, the reaction mixture was refluxed for 16 hours, cooled and acidified with dilute (1:1) hydrochloric acid. The dark red solution was diluted with 500 ml of water, extracted with ether and the combined ether extracts were dried and distilled. The products obtained were 5.85 grams (9% recovery) of hexafluoropentanediol, b.p. 75-97°C(0.09mm), 28.9 grams (36.3%) of 5-(2-cyanoethoxy)-2,2,3,3,4,4-hexafluoro-1-pentanol, b.p. 108°C (0.08 mm), n_D^{20} 1.3950-1.3958 and 25.2 grams (26.5%) of 1,5-bis(2-cyanoethoxy)-2,2,3,3,4,4-hexafluoropentane, b.p. 165°C (0.08 mm), n_D^{23} 1.4038-1.4042. Identification of the products is based on their infrared spectra.

5. Hydrolysis of 1,5-bis(2-cyanoethoxy)-2,2,3,3,4,4-hexafluoropentane.

(a) Basic Hydrolysis. In a stoppered flask, 10 grams of 1,5-bis(2-cyanoethoxy)-2,2,3,3,4,4-hexafluoropentane were shaken with 50 ml of 10% sodium hydroxide solution until the mixture became homogeneous (2 days). The basic solution was extracted with ether and then acidified with concentrated sulfuric acid. Ether extraction followed by evaporation of the ether gave 6.15 grams of 2,2,3,3,4,4-hexafluoro-1,5-pentanediol, m.p. 73-77.5°C. When the flask containing the sodium hydroxide solution was first opened after shaking for two days the odor of ammonia was very evident.

(b) Acidic Hydrolysis

(1) A 100 ml three-neck flask was fitted with a condenser, stirrer, and thermometer. Into the flask were placed 10 grams of 1,5-bis(2-cyanoethoxy)-2,2,3,3,4,4-hexafluoropentane and 50 ml of concentrated hydrochloric acid. The mixture was heated at 65-70°C for 8 hours and then warmed to 90°C for one half hour. The volatile components were removed by distillation at approximately 25 mm Hg from a water bath maintained at 50-55°C. The residue was extracted with ether, the ether solution dried over magnesium sulfate, and evaporated to leave an orange oil which would not crystallize. Distillation under reduced pressure produced only a small amount of 2,2,3,3,4,4-hexafluoro-1,5-pentanediol. The bulk of the product was a black oil and tar.

(2) Ten grams (0.0296 mole) of 1,5-bis(2-cyanoethoxy)-2,2,3,3,4,4-hexafluoropentane was placed in a flask with 25 ml of water and 35 ml of concentrated sulfuric acid. The solution was heated to 100° for one and a half hours and then stirred at room temperature overnight. The slightly discolored solution was poured over 300 grams of ice and the resulting solution extracted with three 100-ml portions of ether. The combined extracts were dried over magnesium sulfate and the ether removed by distillation. The solid residue was recrystallized from benzene to give 5.0 grams (78%) of 2,2,3,3,4,4-hexafluoro-1,5-pentanediol, m.p. 70-76°C, mixed m.p. with authentic sample, 72-77°C.

6. Preparation of 1,5-bis(carbethoxymethoxy)-2,2,3,3,4,4-hexafluoropentane. A one-liter three-neck flask was fitted with a Hershberg type stirrer, condenser and thermometer. A solution of 21.2 grams (0.10 mole) 2,2,3,3,4,4-hexafluoro-1,5-pentanediol in 600 ml of dry dioxane was then placed in the flask and 4.6 grams (0.20 mole) of metallic sodium was added. The mixture was heated with rapid stirring until the sodium melted and then cooled slightly until most of the resulting sodium sand had reacted. After no further apparent reaction of the sodium, the mixture was refluxed for an hour. Slowly, 33.4 grams (0.20 moles) of ethyl bromoacetate was added and the reaction mixture maintained at 90-100°C for 13 hours. Most of the dioxane was then removed by distillation under reduced pressure from a warm water bath. The residual solid and oil were poured into 200 ml of cold water, made slightly acidic with dilute sulfuric acid and extracted with ether. The ether extracts were washed with dilute sodium hydroxide to remove any unreacted diol and dried over magnesium sulfate. After removal of the ether, the residue was distilled through a 25 cm packed column to give 2.6 grams 2,2,3,3,4,4-hexafluoro-1,5-pentanediol, b.p. 75-79°C (0.2 mm), 4.0 grams of a cloudy liquid, b.p. 90-112°C (0.07 mm) n_D^{20} 1.3902-1.3909, and 10.65 grams of a liquid, b.p. 112°C (0.07 mm) - 140° (0.4 mm), n_D^{20} 1.3937-1.4100. This latter liquid was combined with a similar fraction from a previous run and redistilled through a packed column to give 8 grams, b.p. 98-133°C (0.1 mm), n_D^{20} 1.3888-1.4002 and 13.20 grams of 1,5-bis(carbethoxymethoxy)-2,2,3,3,4,4-hexafluoropentane, b.p. 133-135°C (0.1 mm), n_D^{20} 1.4010-1.4011.

Anal. Calculated for $C_{13}H_{18}F_6O_6$: C, 40.63; H, 4.72; M_R, 69.58 (bond refractivities), 69.68 (Eisenlohr values).

Found: C, 40.93; H, 4.50; M_R, 69.40.

7. Preparation of 1,5-bis(Carboxymethoxy)-2,2,3,3,4,4-hexafluoropentane. A three-neck flask of 100 ml capacity was fitted with a thermometer, stirrer and simple distilling head connected to a downward condenser. Into the flask were placed 6.0 grams (0.0156 mole) 1,5-bis(carbethoxymethoxy)-2,2,3,3,4,4-hexafluoropentane and 50 ml of 90% formic acid. The flask was then heated to 102°C and left at that temperature overnight. The excess formic acid was then removed by distillation at reduced pressure from a water bath maintained at 55-70°C. The residual oil solidified on cooling and was recrystallized from toluene containing a small amount of diisopropyl ether to yield 3.90 grams (76%) of 1,5-bis(carboxymethoxy)-2,2,3,3,4,4-hexafluoropentane, m.p. 81-82.5°C. Neutral equivalent calculated, 164.1; found, 165.3 and 165.4.

8. Preparation of 1-(2-Carbomethoxyethoxy)-2,2,3,3,4,4-hexafluoro-5-pentanol. To a solution of 11.0 grams (0.052 mole) of 2,2,3,3,4,4-hexafluoro-1,5-pentanediol in 50 ml of dioxane, 0.1 gram (0.0043 mole) of metallic sodium was added and the mixture heated to reflux until the sodium was all dissolved. After cooling to room temperature, 12.9 grams (0.15 mole) of methyl acrylate (stabilized with hydroquinone) was added and the mixture was heated to reflux for 4 hours while being stirred vigorously. Most of the dioxane and unreacted methyl acrylate were then removed by distillation and the residue was poured into 300 ml of cold water. The aqueous solution was

made acidic with sulfuric acid and extracted with three 75 ml portions of ether. The combined extracts were washed with 10% sodium carbonate and dried over magnesium sulfate. The ether was removed and the residual yellow liquid was distilled to yield 3.45 grams (31% recovery) of the hexafluoropentanediol, b.p. 75-90°C (0.1 mm), and 5.95 grams of impure 1-(2-carbomethoxyethoxy)-2,2,3,3,4,4-hexafluoro-5-pentanol, b.p. 97-109°C (0.2 mm), n_D^{20} 1.3892. Refractionation produced a pure sample, b.p. 111°C (0.45 mm), n_D^{20} 1.3900.

Anal. Calculated for $C_9H_{12}F_6O_4$: C, 36.25; H, 4.06.

Found: C, 36.19; H, 4.29.

C. NITROGEN-CONTAINING MONOMERS

1. Preparation of Ethyl 3-Methylamino-4,4,5,5,6,6,6-heptafluorohexanoate. Into a combustion tube were placed 52.6 grams (0.20 mole) of ethyl 4,4,5,5,6,6,6-heptafluoro-2-hexenoate and 3.1 grams (0.10 mole) of anhydrous methylamine. The tube was sealed and heated at 100°C for 36 hours. The contents were fractionated to give 22.6 grams (42% recovery) of unreacted α,β-unsaturated ester and 25.6 grams (86% based on methylamine) of ethyl 3-methylamino-4,4,5,5,6,6,6-heptafluorohexanoate, b.p. 88°C (20 mm), n_D^{28} 1.3574.

Anal. Calcd. for $C_9H_{12}F_7O_2N$: C, 36.13; H, 4.04; N, 4.68.

Found: C, 36.20; H, 4.04; N, 5.00.

2. Attempted Reaction of Ethyl 3-Methylamino-4,4,5,5,6,6,6-heptafluorohexanoate with Ethyl 4,4,5,5,6,6,6-Heptafluoro-2-hexenoate. The 3-methylamino ester (29.9 grams, 0.10 mole) and 26.8 grams (0.10 mole) of the α,β-unsaturated ester were heated in a sealed tube at 140°C for 10 hours and then 175°C for 5 hours. Fractionation of the contents gave 26.7 grams (~ 100% recovery) of the α,β-unsaturated ester and 11.9 grams (37% recovery) of the amino ester and 7.6 grams of a yellow liquid, b.p. 82-85°C (1.0 mm) which solidified on standing. The latter substance contains fluorine and nitrogen but is not acidic and does not give a test for an ester.

3. Attempted Reaction of Ethyl 3-Methylamino-4,4,5,5,6,6,6-heptafluorohexanoate with Ethyl Bromoacetate. In a 3-neck flask fitted with stirrer, condenser and thermometer, 8.97 grams (0.03 mole) of the 3-methylamino ester, 5.0 grams (0.03 mole) of ethyl bromoacetate and 5.0 grams (0.36 mole) of anhydrous potassium carbonate were heated at 140°C for 2.5 hours. The dark brown reaction mixture was diluted with water and the organic matter taken in ether. The ether solution was dried, evaporated and the residue fractionated to obtain 3.55 g. (39% recovery) of the amino ester and 2.65 grams of a slightly yellow liquid, b.p. 75-77°C (0.5 mm), n_D^{20} 1.4078-1.4088.

The latter substance contains fluorine and nitrogen and gives a test for an ester.

D. CARBON-CHAIN MONOMERS

1. Preparation of Perfluoroglutaric Acid. In a five-liter three-necked flask fitted with a stirrer and condenser were placed 369 grams (1.5 moles) of 1,2-dichlorohexafluorocyclopentene, 333 grams (2.1 moles) of potassium permanganate, 225 grams (4.05 moles) of potassium hydroxide and 1000 grams of water. The mixture was heated to boiling and refluxed for 21 hours. Steam distillation allowed recovery of 36.4 grams (9.86%) of unreacted dichlorohexafluorocyclopentene. The dark-colored reaction mixture was then acidified with 630 ml of concentrated sulfuric acid in 750 grams of water and sulfur dioxide was bubbled through the mixture until all the manganese dioxide dissolved. The aqueous solution was extracted with four 200 ml portions of ether. The ether and aqueous solutions were combined with the corresponding solutions from a similar preparation made on 123 grams (0.5 mole) of the dichlorohexafluorocyclopentene. The aqueous solution was extracted continuously with ether for 42 hours and this new ether solution was combined with the former ether solution and dried over Drierite. After removal of the ether by distillation at atmospheric pressure the residual oil was distilled at 1 mm to give 374 grams (86% yield, 78% conversion) of impure perfluoroglutaric acid, b.p. 114-121°C (1.0 mm). The majority of the product was white but the latter part collected was at first light pink and then yellow in color.

2. Preparation of Diethyl Perfluoroglutarate. Into a three-liter flask were placed 480 grams (2.0 moles) perfluoroglutaric acid, 400 grams (8.7 moles) of absolute ethyl alcohol, 1370 grams of dry benzene and 33.3 grams (0.34 mole) concentrated sulfuric acid. The solution was refluxed and water and ethyl alcohol were removed by way of a Dean-Stark trap. Refluxing was continued for 18 hours. The acidic solution was cooled somewhat and 19.6 grams (0.34 mole) of calcium oxide were added. After refluxing an additional hour the suspension was cooled and the calcium sulfate filtered off. Distillation produced 495 grams (84%) of diethyl perfluoroglutarate, b.p. 76°C (3.0 mm).

3. Preparation of 2,2,3,3,4,4-Hexafluoropentanediol. The reduction of 222 grams (0.75 mole) of diethyl perfluoroglutarate by the method of McBee, Marzluff and Pierce[4] led to 154 grams (96%) of the diol, m.p. 74-8.5°C.

4. Preparation of Perfluoropentanedial. Into a three-liter, three-necked flask fitted with a condenser with drying tube, stirrer and addition funnel with pressure-equalizing side arm were placed 15.0 grams (0.40 mole) of lithium aluminum hydride and one pound of absolute ether. The flask was cooled in a dry ice-trichloroethylene bath and a solution of 222 grams (0.75 mole) diethyl perfluoroglutarate in 500 ml of absolute ether was added over two hours. When the addition was approximately half completed a very thick gel formed and one pound of absolute ether was added through the condenser to break up this gel. The mixture was stirred for an hour after addition was complete. Partial hydrolysis was effected by the dropwise addition of a mixture of 5 ml water, 50 ml dioxane and 50 ml of ether. The reaction mixture was then allowed to warm for several minutes before pouring it into a mixture of 600 grams of ice and 45 ml of concentrated sulfuric acid. The ether layer was removed and the aqueous phase extracted with two 150 ml

portions of ether. The combined ether solutions were dried over magnesium sulfate and the ether was removed by distillation from a warm water bath to yield a cloudy orange liquid.

The residual oil was divided equally, placed into two 1000 ml flasks and 438 ml of 5.25 molar sodium bisulfite solution were added to each flask. The flasks were shaken until a solid phase appeared (about 20 minutes) and were then left overnight. The addition product was filtered off and washed, by forming a thick slurry in a beaker, three times with 500 ml of 95% ethyl alcohol and three times with 500 ml portions of ether. The washed product, which was allowed to air dry overnight, amounted to 223 grams (71% of theory).

The dry sodium bisulfite addition product was placed in a two-liter flask and partially dissolved in 500 ml of water. Approximately half of 130 ml of concentrated hydrochloric acid was added and the mixture was heated slowly to reflux while the remaining hydrochloric acid was added dropwise. Refluxing was continued until there was no more evolution of sulfur dioxide (about three hours).

Most of the water was removed by distillation at 200 mm from a warm water bath. The residue was extracted with four 200 ml portions of ether. The combined extracts were dried and the ether removed by distillation at atmospheric pressure. Distillation of the residue under reduced pressure gave 63.1 grams (40%) of the dialdehyde, b.p. 70-75°C (27 mm), n_D^{20} 1.3671-1.3681. The product, which was water-like in color and viscosity when distilled, increased rapidly in viscosity to finally form a very viscous colorless oil. From the alcohol and ether washings of the sodium bisulfite addition product, 6.2 grams (3.5%) of perfluoroglutaric acid was obtained, b.p. 111-115°C (0.8 mm).

5. Reactions of Perfluoropentanedial with Malonic Acid.

(a) Into a 500 ml 3-necked flask fitted with stirrer, condenser and addition funnel were placed 20.8 grams (0.1 mole) of perfluoropentanedial and 100 ml of toluene. The solution was cooled in an ice bath and 150 ml of pyridine containing 20.8 grams (0.2 mole) malonic acid was added slowly. The ice bath was removed and the reaction mixture was heated to reflux for 2.5 hours. The dark solution was poured into a mixture of 400 grams of ice and 70 ml of concentrated sulfuric acid. The organic phase was removed and the aqueous phase extracted with three 100 ml portions of ether. The combined organic solutions were dried over anhydrous magnesium sulfate and the solvents were removed by distillation under reduced pressure. The residual orange oil was taken up in hot benzene, treated with charcoal and cooled. The crystals which formed amounted to 3.53 grams, m.p. 86-91°C.

(b) The quantities used in this experiment were half those used above. The procedure was the same except that the ether solution of the reaction product was extracted with three 50 ml portions of 10% sodium carbonate solution. The combined extracts were acidified with sulfuric acid then extracted with ether. The ether solution was dried over magnesium

sulfate and the ether removed by distillation. The yellow liquid residue was distilled to give 1.1 grams of an unknown substance, b.p. 64-66°C (2.3 mm), n_D^{20} 1.3946.

(c) In the third experiment the quantities and the procedure used were exactly the same as in the second experiment except that the additional bases Triton B (3 ml) and piperidine (3 ml) were added to the reaction mixture and the reaction mixture was slowly heated to reflux over 14 hours and then refluxed five hours. The product obtained was an orange oil that was only slightly acidic and could not be made to crystallize.

6. Reaction of Perfluoropentanedial with Ethyl Bromoacetate. Into a 500 ml three-necked flask fitted with Hershberg type stirrer, addition funnel and reflux condenser with drying tube attached were placed 5.45 grams (0.0834 mole) of zinc dust. While a stream of dry nitrogen was passed through the apparatus it was hand flamed. When cooled, a solution of 14 grams (0.0834 mole) of ethyl bromoacetate in 50 ml of dry benzene and 80 ml of absolute ether was added and the flask contents were warmed to reflux. Over three-fourths of an hour period of warm solution of 8.7 grams (0.0417 mole) of perfluoropentanedial in 50 ml of dry benzene was added. The reaction mixture was then refluxed for 5.5 hours. After cooling to room temperature, the liquid was decanted from the zinc and the zinc was washed with 50 ml of ether. The combined ether solutions were washed with 50 ml of 10% sulfuric acid, 50 ml of 5% sulfuric acid and 50 ml of water. The combined washings were extracted with two 50 ml of water. The combined washings were extracted with two 50 ml portions of ether and the combined ether solutions were dried over Drierite. Distillation of the residue after removal of the ether gave 1.75 grams of solid material, b.p. 47-49°C (1.0 mm), m.p. 67-75°C, and 2.8 grams of a mixture of solid and dark colored liquid, b.p. 49-80°C (1.0 mm). Sublimation of the solid gave a product which melted at 80-82.5°C. A portion was resublimed and found to melt at 81.5-82.5°C.

7. Preparation of 3,3,4,4,5,5-Hexafluoro-2,6-heptanediol. The Grignard reagent was prepared from 30.35 grams (1.25 mole) of magnesium turnings, 71.0 grams (0.50 mole) of methyl iodide and 92.3 grams (0.75 mole) of isopropyl bromide in 650 ml of ether. While it was being cooled in an ice bath a solution of 74.0 grams (0.25 mole) of diethyl perfluoroglutarate in 200 ml of ether was slowly added. The reaction mixture was stirred at room temperature for 20 hours, poured over 1000 grams of ice and made acidic with dilute hydrochloric acid. The ether layer and ether extracts of the aqueous phase were washed three times with 75 ml of a saturated sodium sulfite solution and dried with anhydrous sodium sulfate. Removal of the ether left a black liquid which was distilled to give 35 grams of highly viscous brown oil, b.p. 76-8°C (0.5 mm). Crystals appeared in several fractions after a few weeks. These crystals were removed and recrystallized several times from benzene to give the pure product, m.p. 79-80.5°C.

Anal. Calcd. for $C_7H_{10}F_6O_2$: C, 35.01; H, 4.19.

Found: C, 35.13; H, 4.38.

E. REPEATED PREPARATIONS FOR ISOLATION OF ADEQUATE AMOUNTS OF INTERMEDIATES AND SAMPLES

1. Preparation of Ethyl Perfluorobutyrate. Perfluorobutyric acid was esterified in the same manner as reported earlier[1]. The combined crude ester from two five-mole reactions yielded 2226 grams (92%) of pure ester, b.p. 94°C.

2. Preparation of Perfluorobutyraldehyde. Reduction of ethyl perfluorobutyrate with lithium aluminum hydride was carried out under the same conditions as reported previously[1] for preparation of perfluorocaprylaldehyde. Three four-mole reductions gave 72%, 76%, and 80% yields of perfluorobutyraldehyde.

3. A New Synthesis of 3-Hydroxy-4,4,5,5,6,6,6-heptafluorohexanoic Acid. Into a three-liter three-neck flask fitted with stirrer, addition funnel and reflux condenser connected to a dry ice trap were placed 341 grams (1.72 mole) perfluorobutyraldehyde and 400 ml of toluene. The flask was immersed in an ice bath and an ice cold solution of 193 grams (1.85 mole) malonic acid in 1000 ml of pyridine was added with vigorous stirring. This resulted in a slush of polymerized aldehyde in the toluene-pyridine solution. (If addition of the pyridine solution is attempted at room temperature the aldehyde polymerizes to form a film over the inner surface of the entire apparatus). The ice bath was then removed and the reaction mixture slowly heated to reflux. Refluxing was continued for three hours--until the evolution of carbon dioxide ceased.

The cooled reaction mixture was then poured over a mixture of approximately 4000 grams of ice and 500 ml of concentrated sulfuric acid. The toluene layer was removed and the aqueous layer extracted with three 300-ml portions of ether. The toluene and ether extracts were combined and dried over anhydrous magnesium sulfate. The ether and most of the toluene were removed by distillation under reduced pressure from a water bath. The residual orange oil was taken up in approximately 1500 ml of hot benzene, treated with charcoal, filtered and allowed to cool. The product amounted to 389 grams (88%), m.p. 78-80°C.[6]

4. Preparation of Ethyl 3-Hydroxy-4,4,5,5,6,6,6-heptafluorohexanoate.

(a) The reaction of perfluorobutyraldehyde with ethyl bromoacetate in the presence of zinc was conducted the same way as previously reported[6]. From two moles of perfluorobutyraldehyde was obtained 150 grams (40%) ethyl 3-hydroxy-4,4,5,5,6,6,6-heptafluorohexanoate, b.p. 89-91.5°C (15 mm), n_D^{21} 1.3532.

(b) Into a 5 liter flask were placed 550 grams (2.13 moles) 3-hydroxy-4,4,5,5,6,6,6-heptafluorohexanoic acid and 2278 grams (49.6 moles) absolute alcohol. Dry hydrogen chloride was bubbled through the solution until 22 grams (0.6 mole) had been absorbed. The flask was stoppered and allowed to remain at room temperature for two days. The reaction mixture was refluxed for four hours and the excess alcohol, water and hydrogen

chloride were removed at reduced pressure. Distillation of the residue gave 517.5 grams (86%) of the β-hydroxy ester, b.p. 92-3°C (15 mm) n_D^{20} 1.3539.

From the still pot residue 8.5 grams of unreacted β-hydroxy acid were recovered.

5. Preparation of Ethyl 4,4,5,5,6,6,6-Heptafluoro-2-hexenoate. The dehydration of ethyl 3-hydroxy-4,4,5,5,6,6,6-heptafluorohexanoate with phosphorus pentoxide was conducted as previously reported[6]. From 517.5 grams (1.81 moles) of the β-hydroxy ester there resulted 325 grams (70%) of the α,β-unsaturated ester and 23.2 grams (5.4%) of 4,4,5,5,6,6,6-heptafluoro-2-hexenoic acid.

6. Preparation of Diethyl 3,5-bis(Perfluoropropyl)-4-thiapimelate and Ethyl 3-Mercapto-4,4,5,5,6,6,6-heptafluorohexanoate. The reaction of hydrogen sulfide with ethyl 4,4,5,5,6,6,6-heptafluoro-2-hexenoate was carried out as reported previously[1]. From 268 grams (1.0 mole) of the α,β-unsaturated ester there were obtained 195.5 grams (68%) of the thiapimelic ester and 56.3 grams (18%) of the mercapto ester. Refractionation of the latter compound gave an analytical sample, b.p. 61°C (4.1 mm), n_D^{22} 1.3747.

Anal. Calcd. for $C_8H_9F_7O_2S$: C, 31.82; H, 3.00.

Found: C, 32.09; H, 2.96.

7. Preparation of 3,5-bis(Perfluoropropyl)-4-thiapimelic Acid. A one-liter three-necked flask was fitted with a thermometer, Teflon stirrer and a 25-cm Vigreux column attached to a simple still head and condenser. Into the flask were placed 195 grams (0.343 mole) diethyl 3,5-bis(perfluoropropyl)-4-thiapimelate and 100 ml of 90% formic acid (2.56 moles, 274% excess). The two phases were stirred vigorously while being heated at 104-105°C for 79 hours. No distillate was collected and no characteristic odor of ethyl formate could be detected. The mixture was then poured into 1000 grams of ice and water. The unreacted ester was separated and the aqueous phase extracted with three 100 ml portions of ether. The combined ether extracts and ester phase were dried over anhydrous magnesium sulfate and the ether was removed by distillation. The residue was dissolved in 400 ml of concentrated sulfuric acid and heated on a steam bath for 45 minutes. The dark red solution was then poured over 2000 grams of ice. The aqueous layer was decanted from the sticky solid thus produced and the solid was taken up in 150 ml of ether. The aqueous solution was extracted with three 200 ml portions of ether and the combined ether solutions dried over Drierite. After the ether was removed by distillation the residue was taken up in approximately 1500 ml of hot benzene. Upon cooling, 66.5 grams of crystalline 3,5-bis(perfluoropropyl)-4-thiapimelic acid was obtained. Second, third and fourth crops of crystals brought the total yield to 79.4 grams (45%). The remaining benzene solution was fractionated to yield 10.0 grams (5%) of unreacted thiapimelate and 43.4 grams of an acidic liquid assumed to be the half ester-half acid, b.p. 128-132°C (0.5 mm). This corresponds to a yield of 23%.

8. Preparation of 3,5-bis(Perfluoropropyl)-4-thiapimelyl Chloride. The procedure used was the same as that previously reported[1]. From 60.0 grams of the thiapimelic acid there was obtained 56.8 grams (88%) of the slightly yellow acid chloride, b.p. 93°C (1.1 mm) to 96°C (1.6 mm), n_D^{21} 1.3886 - 1.3898. Refractionation gave an analytical sample, b.p. 89°C (1.0 mm), n_D^{21} 1.3889.

Anal. Calcd. for $C_{12}H_6F_{14}O_2Cl_2S$: C, 26.15; H, 1.09; Cl, 12.88.

Found: C, 26.12; H, 1.33; Cl, 12.59.

9. Preparation of 3-Hydroxy-4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-pentadecafluorodecanoic Acid. To an ice cold solution of 159 grams (0.40 mole) of perfluorooctanal in 200 ml of toluene a cold solution of 41.6 grams (0.40 mole) of malonic acid in 275 ml of pyridine was added with vigorous stirring. The resulting slurry of polymerized aldehyde was heated slowly to boiling and refluxed until no further evolution of carbon dioxide could be detected. The reaction mixture was poured over 1 kg of ice and 150 ml of concentrated sulfuric acid, the organic phase removed, and the aqueous phase extracted with ether. The combined organic solutions were dried over magnesium sulfate and the solvents removed by distillation up to 105°C at atmospheric pressure. Five hundred ml of toluene were added, the mixture heated until homogeneous and finally allowed to cool slowly. The crude acid which separated out amounted to 128 grams (68%) and was light yellow in color. A portion of the crude product was recrystallized four times to give a white crystalline product, m.p. 123-123.5°C.

Anal. Calcd. for $C_{10}H_5F_{15}O_3$: C, 26.21; H, 1.10.

Found: C, 25.92; H, 1.13.

10. Preparation of Ethyl 3-Hydroxy-4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-pentadecafluorodecanoate. 3-Hydroxy-4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-pentadecafluorodecanoic acid (90 grams, 0.196 mole) was esterified with a large excess, 618 grams (13.4 moles), of ethanol and 8.0 grams (0.22 mole) of hydrogen chloride. After refluxing for 10 hours, the excess alcohol was removed at slightly reduced pressure and the crude product fractionated to yield 82.3 grams (86%) of the ester, b.p. 97°C/1.9 mm, n_D^{23} 1.3412 (supercooled)[7].

11. Preparation of Ethyl 4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-Pentadecafluoro-2-decenoate. Into a 100 ml round-bottomed flask were placed 75 grams (0.155 mole) of ethyl 3-hydroxy-4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-pentadecafluorodecanoate and 14 grams (0.08 mole) of phosphorus pentoxide. Fractional distillation under reduced pressure gave 47.7 grams (66%) of the α,β -unsaturated ester, b.p. 101°C/18 mm, n_D^{28} 1.3340.

Anal. Calcd. for $C_{12}H_7F_{15}O_2$: C, 30.78; H, 1.51.

Found: C, 30.59; H, 1.57.

12. Preparation of 3-Perfluoropropylglutaric Anhydride. The reaction of thionyl chloride with 3-perfluoropropylglutaric acid was conducted as previously reported[6]. From 12 grams (0.04 mole) of the acid and 24 grams (0.21 mole) of thionyl chloride there were obtained 8.35 grams of impure anhydride, b.p. 83-90°C/0.09 mm. The product was recrystallized three times from benzene (dried over calcium hydride) to produce white crystals, m.p. 48.5-9.5°C.

Anal. Calcd. for $C_8F_7H_5O_3$: C, 34.04; H, 1.78.

Found: C, 34.15; H, 2.00.

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